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FIRST BOOK

OF

Qualitative Chemistry

FOR STUDIES OF WATER SOLUTION AND MASS ACTION.

BY
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PREFACE

To enable the beginner in the qualitative laboratory to deal with chemical change in the light of present studies of WATER SOLUTION and of mass action has been the main purpose in preparing this edition. With this intent the little book has been written anew throughout. It was first published by one of the authors in 1879, and designed then as now for classes taking a short course in qualitative practice.

In this edition, as in the one first issued, the object is not so much analysis as it is chemistry; not detective method for its own sake so much as it is a personal acquaintance with the character of the chemical elements and with the nature of chemical change. A suitable course in qualitative chemistry is found to be a favorable avenue by which to approach the vantage grounds of the science.

An outline of the Periodic System, or of some part of it, is kept in view of the student while he is led to trace the gradation in the reactions of the several elements, and thereby to define the different analytical groups.

Some care has been bestowed, in this edition, as in that of 1879, upon statements of the composition of articles in use in daily life under current popular names. This is done in connection with analytical work bearing directly upon the articles so designated, and providing for their analysis. The qualitative student is proverbially curious as to the composition of materials in common use and this interest is available in laboratory teaching.

and suggest

THE UNIVERSITY OF MICHIGAN,
Ann Arbor, January, 1902.

INTRODUCTORY

1. A study of **qualitative chemistry** is a study of the individual components of matter, especially as to their deportment toward one another. Any portion of matter, whether solid, liquid or gaseous, amorphous, crystalline or cellular, is made up of one or more distinct substances. Thus a handful of iron filings may contain iron and two different oxides of iron, each of these being a distinct substance, a kind of matter which has the same properties wherever found. Such distinct substances or chemical individuals are either complex or simple, the latter being recognized by the fact that when subjected to chemical action their weight either is unaffected or increases, indicating that they may combine with other substances but cannot be split up into less complex constituents. These elements, as they are called, are some seventy in number, and all matter is found to be made up of them and of their combinations in certain fixed proportions, definite and unchanging for each compound.

2. **Equivalent Weights.**—Investigation of the quantities so uniting has brought to light such facts as the following:

1.01 grams hydrogen combine with 8.00 grams oxygen;
1.01 grams hydrogen combine with 3.00 grams carbon;
1.01 grams hydrogen combine with 35.45 grams chlorine;
1.01 grams hydrogen combine with 16.00 grams sulphur.

The tendency of 1.01 grams hydrogen to combine is met by the tendency of 8.00 grams oxygen, or 3.00 grams carbon, or 35.45 grams chlorine, or 16.00 grams sulphur to combine. Each of the quantities in the column at the right is equal in combining capacity to 1.01 grams hydrogen; and it is found that they are also equal among themselves in combining capacity, 3.00 grams carbon uniting with 8.00 grams oxygen, or 35.45 grams chlorine, or 16.00 grams sulphur, and so on.

pressed by these c
simple multiples. The equivalent weigl
then, is that quantity capable of coml
replacing from its compounds a fixed qı
element chosen as the unit.

3. Valence.—The atomic theory assume
expression or picture of the laws of coml
ence of indivisible particles of matter l
weight for each substance. Certain lines o
cannot be taken up here give methods foı
relative weights of these hypothetical sı
These are for the elements the atomic weig
weight is the equivalent weight or its simı
multiple being known as the valence. Tl
element then shows the number of equivalen
in grams) of other substance with which th
(taken in grams) of the element can combiı
is thus a measure of the combining capacity
ties of the elements which are proportional
weights. If the valence of an element is
weight is three times its equivalent weight
weight taken in grams is capable of union
the equivalent weight of any other element
If the valence of this second element is also
times its equival

4. Chemical Notation.—The alphabet of the chemical method of writing is made up of certain symbols representing the elements. These not only serve as abbreviations for the names of the elements, but they are also used to express fixed relative quantities. Each symbol represents the atomic weight of the element taken in some unit of weight—grams, ounces or tons indifferently. Two symbols written side by side indicate a union of the elements in question, and as union takes place in a ratio represented by simple multiples of the equivalent and therefore also of the atomic weights, we can by multiplying our symbols express in this way the quantitative composition of all possible compounds.

The formula for sodium carbonate, Na_2CO_3, expresses the fact that it is a compound from which sodium, carbon and oxygen may be obtained in quantities which are to one another respectively as twice the atomic weight of sodium, the atomic weight of carbon, and three times the atomic weight of oxygen, the figure to the right below the line multiplying that symbol (or group of symbols enclosed in parenthesis) which it immediately follows. Forty-six grams of sodium, twelve grams of carbon, and forty-eight grams of oxygen will therefore give 106 grams of sodium carbonate, and the composition per cent is: 43.4 sodium, 11.3 carbon, 45.3 oxygen.

5. The Equation.—The chemical equation indicates the formation of certain products from certain reacting substances. It shows the relative quantities uniting with one another and resulting from the change.

$$\begin{array}{ccccccc} \mathrm{CaO} & + & 2\mathrm{HCl} & = & \mathrm{CaCl_2} & + & \mathrm{H_2O} \\ 40+16 & & 2(1+35.5) & & 40+2\times 35.5 & & 2\times 1+16 \end{array}$$

Calcium oxide with hydrochloric acid forms calcium chloride and water.

$$\begin{array}{ccccccc} \mathrm{Pb(NO_3)_2} & + & \mathrm{H_2S} & = & \mathrm{PbS} & + & 2\mathrm{HNO_3} \\ 206+2(14+3\times 16) & & 2\times 1+32 & & 206+32 & & 2(1+14+3\times 16) \end{array}$$

Lead nitrate with hydrogen sulphide forms lead sulphide and nitric acid.

The numbers refer to weight units, as milligrams or pounds.

A chemical equation cannot be written without a previous investigation of the reaction on the part of some one. It is impossible to predict the result of bringing two substances together unless the experiment has already been performed. Analogy of course furnishes a clew in many cases, but there is always a possibility of its failing.

Frequently the products of a reaction may, under suitable conditions, act upon one another to form again the substances originally taken. Such reversible reactions are sometimes indicated thus:

$$BaCl_2 + H_2SO_4 \rightleftarrows BaSO_4 + 2HCl \quad \text{or}$$
$$BaCl_2 + H_2SO_4 \rightleftarrows BaSO_4 + 2HCl$$

Reasoning indicates that all reactions are reversible, but in many cases the reversibility has not yet been shown.

6. Salts, Acids and Bases.—Inorganic bodies (those not related in composition to the complex material of organized life) were early recognized to fall into three great classes. Those of one class, when dissolved in water, had a sour taste, were corrosive in their action on organic and mineral substances, and had a characteristic effect on certain vegetable coloring matters. The bodies of the second class, in water solution, had an unpleasant taste, gave the skin a slippery, "soapy" feel, and affected vegetable coloring matter in a manner peculiar to themselves, different from the action of the members of the first class. If the bodies of the first class were brought into contact with those of the second, each lost its peculiar properties and there resulted the substances of the third class; these were by far the most numerous, were rather neutral in character, and usually had in water solution a salty taste. The first class has received the name acids; the second, alkalis or bases; the third, salts. Analysis showed the acids to be compounds of hydrogen with negative (non-metallic) elements or groups, and bases to contain oxygen, or oxygen and hydrogen, united to a positive (metallic) element or group of elements, the terms positive and negative being used simply to indicate contrast in chemical behavior. Further investigation showed the acids to owe their characteristic properties to the hydrogen ion (see §20) and the bases theirs to the hydroxyl ion. The acidity of a solution is in proportion to the concentration of the hydrogen ions which it contains, and its basicity to the concentration of its hydroxyl ions. Salts contain both the positive and the negative constituent, part or all of the hydrogen of the acid (the hydrogen ions) and of the oxygen and hydrogen of the base (the hydroxyl ions) having separated as water. The part of the acid going into the salt is called the acid radical; that portion of the base found in the salt is correspondingly the basic radical.

The formation of a salt may be regarded as the substitution of the hydrogen of an acid by an equivalent quantity of metal. It may also be regarded as the substitution of the oxygen, or oxygen and hydrogen, of a base by a non-metal or non-metallic group.

An acid is mono-, di-, or tribasic, according as its formula is written with one, two or three equivalents of replaceable hydrogen. The number of hydrogen equivalents with which the acid radical is so combined gives of course the valence of the acid radical.

A normal or neutral salt is one in which the replaceable hydrogen of an acid has been exactly substituted by metal. In an acid salt but part of the acid hydrogen has been replaced by metal, while a basic salt is one in which the ratio of base to acid is greater than in a normal salt. But a normal or so-called neutral salt may have acid or alkaline reaction when dissolved in water; in fact, acid salts are sometimes alkaline and basic salts sometimes acid in their reaction to indicators. This depends upon the presence of hydrogen or hydroxyl ions and will be discussed under hydrolysis.

“ate” or “ite” according as the nam
“ic” or “ous”:

HCl	hydrochloric	acid,	forming
$HClO_3$	chloric	“	“
HBr	hydrobromic	“	“
$HBrO_3$	bromic	“	“
HI	hydriodic	“	“
HIO_3	iodic	“	“
HNO_3	nitric	“	“
H_2S	hydrosulphuric	“	“
H_2SO_3	sulphurous	“	“
H_2SO_4	sulphuric	“	“
H_2CO_3	carbonic	“	“
H_2CrO_4	chromic	“	“
H_3PO_4	phosphoric	“	“
Organic acids:			
$HC_2H_3O_2$	acetic	“	“
$H_2C_2O_4$	oxalic	“	“

The anhydride of an oxyacid may be
acid by removal of water; in most case
obtained from its anhydride by addition
the anhydride of H_2SO_4; CO_2 is the anh
P_2O_5 is the anhydride of

valence. See §3.) The chlorine of HCl is monovalent (shown in the formula of the acid by its combining with one equivalent of hydrogen) and the symbol Cl represents its equivalent weight as well as its atomic weight. The formula NaCl therefore gives us the elements in equivalent quantities and indicates the composition of their compound. The symbol Ba for barium, divalent, stands for twice its equivalent weight and the quantity represented by the symbol therefore requires for union two equivalent weights of chlorine, and the formula for their compound is $BaCl_2$. The radical PO_4 of H_3PO_4 is trivalent, the formula of the acid showing that the radical combines with three equivalent weights of hydrogen. The symbol PO_4 represents three equivalent weights, the symbol Ba two. Equivalence is obtained by taking two PO_4 ($2 \times 3 = 6$) and three Ba ($3 \times 2 = 6$), and the formula for their compound is written $Ba_3(PO_4)_2$.

In the following the valence of the basic constituent is indicated by $^{\cdot}$, of the acid constituent by $'$:

$K^{\cdot}$	forms with	HNO_3	$K^{\cdot}(NO_3)'$	potassium nitrate
$K^{\cdot}$	" "	H_2SO_4	$(K_2)^{\cdot\cdot}(SO_4)''$	potassium sulphate
$K^{\cdot}$	" "	H_3PO_4	$(K_3)^{\cdot\cdot\cdot}(PO_4)'''$	potassium phosphate
$Ca^{\cdot\cdot}$	" "	HCl	$Ca^{\cdot\cdot}(Cl_2)''$	calcium chloride
$Ca^{\cdot\cdot}$	" "	H_2SO_4	$Ca^{\cdot\cdot}(SO_4)''$	calcium sulphate
$Ca^{\cdot\cdot}$	" "	H_3PO_4	$(Ca_3)^{\cdot\cdot\cdot\cdot\cdot\cdot}(PO_4)_2''''''$	calcium phosphate
$Bi^{\cdot\cdot\cdot}$	" "	HCl	$Bi^{\cdot\cdot\cdot}(Cl_3)'''$	bismuth chloride
$Bi^{\cdot\cdot\cdot}$	" "	H_2SO_4	$(Bi_2)^{\cdot\cdot\cdot\cdot\cdot\cdot}(SO_4)_3''''''$	bismuth sulphate
$Bi^{\cdot\cdot\cdot}$	" "	H_3PO_4	$Bi^{\cdot\cdot\cdot}(PO_4)'''$	bismuth phosphate

The acid radical and basic radical will be equivalent, capable of union without leaving an excess of either, when the valence of the one is equal to the valence of the other, as in the above cases.

For practice, let the student write the formulas for the normal salts formed by each of the following metals with each of the following acids:

$Na^{\cdot}$	HCl
$Mg^{\cdot\cdot}$	H_2SO_4
$Bi^{\cdot\cdot\cdot}$	H_3PO_4

the metallic state, nor that ch
in common salt by producing chlorine ga
a reliable and accurate method of analysis
that analyses originally were made. But
another course of procedure is equally tr
more convenient, and this lies in the prod
elements themselves, but of one or more o
istic reaction-products. The task of the a
sists in subjecting the substance investigat
tions that the element sought will, if pres
mistakably by the formation of a compound
or having distinctive solubilities in various
favorable conditions are brought about
change in physical conditions, as by applying
heat or varying the pressure, but more freq
ing the unknown body into contact with som
substance. This is conveniently, although n
in water solution, as intimate contact is thu
in addition, the activity of most substances
dissolving in water.

10. Reagents.—Chemicals thus used for
producing characteristic changes in a mix
reagents. It is to be noted that reagents
a peculiar class of chemical compounds
stances

of dissolved substance (solute) which are equivalent to one another, that is, equal in combining capacity, are of great convenience in qualitative as well as quantitative work, and it is advisable to adjust the concentration of reagents by some such plan. Where the equivalent weight in grams is contained in one liter of solution the solution is said to be of *normal* strength.* If there is half the equivalent weight in grams in a liter the solution is *half-normal* (½N or N/2); if five times the equivalent weight is present in a liter the solution is *five-normal* (5N), and so on.

The equivalent weight of a neutral salt is that quantity which contains the equivalent weight of acid and basic radical. For Na_2CO_3 a normal solution contains the equivalent weight (53 grams) in one liter. A half-normal solution, made from the normal solution by diluting with an equal volume,† or from the five-normal solution by diluting with nine volumes of water, contains 26.5 grams Na_2CO_3 per liter. A half-normal solution of $BaCl_2$ contains 52 grams per liter of the anhydrous salt or 61 grams per liter of the crystalline $BaCl_2,2H_2O$. Ten cubic centimeters of N/2 Na_2CO_3 (containing 0.265 gram Na_2CO_3) are just sufficient to precipitate ten cubic centimeters of N/2 $BaCl_2$ (0.520 gram $BaCl_2$), as these are the relative quantities indicated by the equation $BaCl_2 + Na_2CO_3 = BaCO_3 + 2NaCl$.

For use in the University of Michigan laboratory, the acids and alkalis are made 5N, Na_2CO_3 3N, other reagents and side-table solutions for the most part ½N. See list of reagents, §252.

12. Manipulation.—Upon care in the use of reagents will depend very largely success or failure in analytical work. It must be borne in mind that intelligent thought is fully as essential to the successful chemist as are test-tubes and funnels. The student is urged to cultivate the habit when using a reagent of forming a mental picture of *all* the substances in the two solutions and the probable results of bringing them together. In other words, *think always!*

---

* The word "normal" is used here in a sense which is quite independent of its use in the term "normal salt."

† For strict accuracy the dilution in the two cases cited would be to twice the original volume and ten times the original volume. The volume of a mixture of two liquids is in general not exactly the sum of the original volumes.

Liquid reagents should be added a little at a time, as a rule until no further change is produced. Not only economy, but accuracy also is favored by a sparing use of materials. In adding either acids or alkali hydroxides to dissolve precipitates, the liquids should be used in small quantity, so as to be as nearly saturated as possible. Applied to a solution, they should in most cases be used in just sufficient quantity to impart acid or alkaline reaction respectively, always to be tested with litmus.

Where a test depends upon the production of a precipitate, the solution examined and the reagent used must be absolutely clear—not necessarily colorless, but free from suspended particles. If they are not so, they must be filtered. Where doubt exists as to whether or not precipitation has been produced, compare in test-tubes with an equal bulk of distilled water, or better of the solution to which the reagent has not been added. Any precipitate which the eye can detect is sufficient evidence of the substance sought if other matter has been carefully excluded. Filter-paper fiber must not be mistaken for a precipitate. Do not neglect traces. The work is far more satisfactory, and on the whole less difficult, if very slight precipitates as well as the heavier ones are given full attention.

A solution should, in general, be warmed after addition of a reagent, rise of temperature in all cases without exception hastening chemical action; it should then be cooled before filtering, as most precipitates are less soluble cold than hot. The filtrate, if it is to undergo further examination, must always be tested as to the completeness of the precipitation by addition of a small quantity of the precipitating agent and warming.

The importance of thorough work with the known substances before attempting analysis of mixtures of unknown composition cannot be too strongly emphasized. Never make a test in an unknown without previously having made the same test where the substance sought was known to be present and again where it was known to be absent. If the unknown gives ambiguous results go back to the solution known to contain the substance suspected and work the two side by side, comparing results.

It is desirable to know approximately the delicacy of the tests used—the least quantity of the substance which can be found by their aid. This is ascertained by diluting say one cubic centimeter of N/2 solution, measured in the pipette, with nine cubic centimeters of water, giving N/20 solution. The test is made in a part of this, and if successful one cubic centimeter of the dilute solution is mixed with nine cubic centimeters of water, giving ten cubic centimeters of N/200 solution, a part of which is tested as before; the dilution and testing are continued until finally a solution is obtained so dilute that it fails to give the reaction.

13. The Analytical Groups.—When the components of a little-soluble substance are brought together in solution, so much of the substance separates out (precipitates) as is in excess of the quantity required for a saturated solution. (See definition of saturated solution under "Solubility.") In separation of metals (kathions) or acids (anions) from one another, by a suitable selection of reagents certain of them may be removed by precipitation and others left in solution. Those precipitated together make up an analytical "Group." By the successive addition of certain reagents, each time completing and removing the precipitate produced, the metals are, in systematic analysis, divided into six such groups. This division is merely one of convenience, those reagents being chosen which give complete precipitation of mixtures lending themselves readily to further treatment. The six groups, with the reagents to which the grouping is due, are:

I. Silver Group, precipitated by HCl:
  Silver, $Ag^{\cdot}$
  Lead, $Pb^{\cdot\cdot}$
  Monovalent mercury, $Hg^{\cdot}$

II. Tin and Copper Group, precipitated by H_2S in slightly acid solution: *
 The Tin Subgroup—
  Arsenic, $As^{\cdot\cdot\cdot}$ and $As^{\cdot\cdot\cdot\cdot\cdot}$
  Antimony, $Sb^{\cdot\cdot\cdot}$ and $Sb^{\cdot\cdot\cdot\cdot\cdot}$
  Tin, $Sn^{\cdot\cdot}$ and $Sn^{\cdot\cdot\cdot\cdot}$
 The Copper Subgroup—
  Divalent mercury, $Hg^{\cdot\cdot}$
  Lead, $Pb^{\cdot\cdot}$
  Bismuth, $Bi^{\cdot\cdot\cdot}$
  Copper, $Cu^{\cdot\cdot}$
  Cadmium, $Cd^{\cdot\cdot}$

III. Iron Group, precipitated by NH_4OH in presence of NH_4Cl:
  Iron, $Fe^{\cdot\cdot\cdot}$
  Aluminum, $Al^{\cdot\cdot\cdot}$
  Chromium, $Cr^{\cdot\cdot\cdot}$

IV. Zinc Group, precipitated by $(NH_4)_2S$:
  Cobalt, $Co^{\cdot\cdot}$
  Nickel, $Ni^{\cdot\cdot}$
  Manganese, $Mn^{\cdot\cdot}$
  Zinc, $Zn^{\cdot\cdot}$

V. The Alkaline Earth Metals:

$$\left.\begin{array}{l}\text{Barium, Ba}^{\cdot\cdot}\\ \text{Strontium, Sr}^{\cdot\cdot}\\ \text{Calcium, Ca}^{\cdot\cdot}\end{array}\right\}\text{ precipitated by }(NH_4)_2CO_3$$

  Magnesium, $Mg^{\cdot\cdot}$, precipitated by Na_2HPO_4

---

* The metals of the silver group, if present, will be precipitated by this reagent. And in general the reagent of each group will precipitate the other groups preceding it in this plan of separation.

VI. The Alkali Group, not precipitated:
Ammonium, $NH_4^{\cdot}$
Sodium, $Na^{\cdot}$
Potassium, $K^{\cdot}$

This grouping, with the valence of each of the metals, should be memorized.

14. Electrolytic Dissociation.—A water solution of hydrochloric acid is found to contain the acid in two different forms, one decidedly more active than the other. The active form has the power of carrying the electric current, it enters readily into chemical action, exchanging its hydrogen or its chlorine for other substances, and it exerts twice as great osmotic pressure * as the same quantity of hydrochloric acid in the inactive form. The inactive form is practically a non-conductor of electricity and is perfectly passive chemically, having none of the characteristics of an acid. Measurement of the power of conducting the electric current, of the chemical activity, or of the osmotic pressure gives the relative quantities of active and inactive acid present in any hydrochloric solution.

These facts are interpreted in the Theory of Electrolytic Dissociation by the assumption that in the active acid the hydrogen and chlorine are not bound firmly to each other as in the inactive acid, but are present in a condition in which they are to some extent mutually independent, each being capable of carrying electricity, each adding to the osmotic pressure as an individual, and each, owing to its independence, readily entering into combination or exchange with other substances. The hydrogen and chlorine in this state are called *ions*. This is true not only of hydrochloric acid, but of all acids, bases and salts in water solution. When we say that a substance is partly dissociated into its ions in water solution we simply give a name to that portion of it which measurement of certain physical and chemical properties shows to be more active than the other, so-called non-dissociated portion.

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* The pressure by virtue of which a soluble substance in contact with the solvent, as common salt in water, is enabled to rise against the force of gravity and distribute itself uniformly throughout the solvent, just as a gas by virtue of the gas-pressure occupies the entire space at its disposal.

In this breaking up into the ions we have an explanation of the comparative simplicity of the analysis of inorganic substances. In an examination for barium chloride, for instance, the test is made not for the salt as such, but with sulphuric acid for the barium ion and with silver nitrate for the chloride ion. Thus, as Ostwald points out, instead of 2500 different reactions given by the combination of fifty bases with fifty acids, we have only 100—fifty for the basic or positive ions and fifty for the acid or negative ions. *The reactions in water solution are reactions of the ions.*

The chemical activity of a substance is therefore in proportion to the extent of its dissociation into ions, and the neutral salts and strong acids and bases, the substances which are most active chemically, exist in water solution for the most part in the dissociated condition, the molecules of sodium nitrate, for instance, splitting up into $Na^{\cdot}$ and NO_3', hydrochloric acid into $H^{\cdot}$ and Cl', potassium hydroxide into $K^{\cdot}$ and OH'.* The normal salts are practically completely ionized, 80 to 90 per cent of the total quantity being present as the ions in solutions of ordinary strength. There are a few exceptions, most prominent among these being the very slightly dissociated salts formed by $Hg^{\cdot\cdot}$ with hydracids. Salts consisting of monovalent ions, as $NaCl$ and NH_4NO_3, are slightly more dissociated than others. Ranking with these in extent of dissociation are the strong acids and bases. The former owe their acid activity to the H ion and the latter their basic activity to the OH ion. The activity in these cases, as in all others, is numerically proportional to the concentration of the ions concerned, that is, to their number in unit volume.

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* *A chemical symbol with the dot indicates a kathion, with the accent an anion; the number of dots or accents gives the valence.* The kathion is the positive or basic ion, which carries positive electricity and moves toward the kathode (the negative electrode) when a current is passed through the solution; the anion, the negative ion, moves in the opposite direction.

The anion of a neutral salt, as $NaNO_3$, is identical in composition with the acid radical, that is, it contains the same elements in the same relative quantities. But the acid radical includes all of the nitrogen and oxygen of nitric acid or a nitrate while the anion is only the more active portion, assumed by the theory of electrolytic dissociation to be in a comparatively independent state and to carry a charge of negative electricity. Chlorine the ion is not to be confounded with chlorine, monatomic, in the free state. The two are quite unlike. Free chlorine to form the chlorine ion, of sodium chloride, for instance, must undergo two energy changes, first on combining with sodium to form non-dissociated sodium chloride, and again on changing from non-dissociated sodium chloride to the ion; and a change in the energy content of a substance is sufficient to bring about entire change in its properties and behavior, as in the case of red and yellow phosphorus, or of an element in the free and in the combined state. In addition, the chlorine ion is supposed to be electrically charged and it can scarcely exist except in the presence of another ion with equal charge of opposite sign.

The strong acids, which rank with the salts in extent of dissociation, are HCl, HBr, HI, HNO_3, $HClO_3$, $HClO_4$, H_2SO_4, and the polythionic acids.

Acids of medium strength are H_3PO_4, H_2SO_3, $HC_2H_3O_2$, with dissociation usually not exceeding ten per cent.

Weak acids, dissociated to less than one per cent, are H_2CO_3, H_2S, HCN, H_2SiO_3, H_3BO_3.

The hydroxides of the alkali and alkaline earth metals are strong bases, dissociated in about the same amount as the neutral salts and strong acids.

Bases of medium strength are ammonium hydroxide, silver oxide, magnesium hydroxide. The hydroxides of other metals are weakly basic. (Ostwald.)

The student will do well to memorize these divisions.

Electrolytic dissociation is made greater by dilution; acetic acid, for instance, is about 1% dissociated into the ions $H^{\cdot}$ and $C_2H_3O_2'$ in normal solution, and about 10% dissociated in hundredth-normal solution.

15. Chemical Equilibrium.—Equilibrium among chemical substances at a given temperature exists only when they are present in a certain fixed relative quantity per unit volume. The quantity of a substance in unit volume, the total quantity (expressed in gram molecular weights) divided by the volume occupied, is the concentration.[*] Every chemical reaction is a decrease in relative concentration of some substances and an increase in relative concentration of others in the striving of the components of a system to come into equilibrium with one another.

Investigation of a large number of reactions has shown that if certain substances A and B react to form certain others C and D, a state of equilibrium is reached in which the product obtained by multiplying together the final concentrations of A and B is equal to a constant quantity times the product obtained by multiplying together the concentrations of C and D. This is represented by the equation $ab = kcd$, in which a and b are the concentrations of substances A and B, c and d those of substances C and D, and k the constant, always the same for the same reaction at a given temperature.[†] This is known as the Law of Mass-Action.

The same equilibrium results whether we start with an excess of A and B or of C and D, that is, reactions are in general reversible, change taking place in either direction according as one substance or another is in insufficient quantity to fulfill the equilibrium conditions.

When sodium chloride solution is added to potassium nitrate solution the resulting mixture contains $Na^{\cdot}$, $K^{\cdot}$, Cl', NO_3', $NaCl$, KNO_3, $NaNO_3$, and KCl in equilibrium with one another; and the solution obtained by bringing together corresponding quantities of sodium nitrate and potassium chloride is identical with this. Sodium acetate added to hydrochloric acid gives the same result as acetic acid added to sodium chloride; the equilibrium is the same whether ammonium chloride is treated with potassium hydroxide or ammonium hydroxide with potassium chloride; barium sulphate and hydrochloric acid form the same products, in the same proportion, as barium chloride and sulphuric acid; and so on indefinitely.

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[*] Two substances are of equal concentration when they have the same number of molecules in a given space, that is, when the quantities in unit volume are to each other as the molecular weights of the substances. H_2SO_4 of unit concentration contains 98 grams in unit volume, one liter. NaOH of unit concentration has 40 grams per liter. $Ba(OH)_2$ containing 34 grams per liter is of concentration 1/5 (34/170), the OH ions, assuming complete dissociation, of concentration 2/5 (6.8/17).

[†] If the reaction involves no absorption or evolution of heat k is independent of the temperature. If the formation of C and D from A and B causes evolution of heat k will increase, if absorption, it will decrease with rising temperature. Higher temperature gives a greater quantity of those substances whose formation absorbs heat, lower temperature increases the quantity of those substances whose formation is attended with evolution of heat. The velocity of the reaction, the rate at which the equilibrium state is approached, is in all cases accelerated by rise of temperature.

16. Methods of making a Reaction Complete.—If from the sodium chloride-potassium nitrate mixture water be removed by evaporation until it is in insufficient quantity to hold all the salts dissolved, that substance will separate which is least soluble under the circumstances. At certain temperatures sodium chloride is less soluble than any of the other three salts present, and it begins to crystallize out. This decreases the quantity of sodium chloride in solution and so disturbs the equilibrium which had existed among the dissolved substances. To restore equilibrium potassium chloride and sodium nitrate react to form sodium chloride and potassium nitrate in such quantity that the former ratio of concentrations is restored. Further evaporation causes crystallization of more sodium chloride, and potassium chloride and sodium nitrate again react to replace it. In this way the dissolved salts may be obtained almost wholly as sodium chloride and potassium nitrate, the latter remaining in solution. The conversion of sodium nitrate and potassium chloride into sodium chloride and potassium nitrate is thus furthered by *removing one of the products of the reaction.*

If conditions could be found in which sodium nitrate or potassium chloride became the least soluble substance the reverse change would take place and transformation into these salts would result. And chemical reactions in general may be made complete by removing from the sphere of action one or more of the resulting substances. The chlorine ion of a dissolved chloride is precipitated practically completely by the silver ion of silver nitrate because the silver chloride formed is almost insoluble and so is removed as rapidly as produced.* Sulphuric acid decomposes sodium chloride completely, with formation of hydrochloric acid and sodium sulphate, because the hydrochloric acid is removed by vaporization—not because sulphuric is a stronger acid. (As a matter of fact sulphuric is the weaker acid of the two.)

A chemical change becomes nearly complete also in case it involves the formation of a slightly dissociated substance. When hydrochloric acid is added to sodium acetate the hydrogen of the acid is mostly taken up to form non-dissociated acetic acid, equilibrium in this case requiring that the non-dissociated portion be large in comparison with the portion ionized as $H^{\cdot}$ and $C_2H_3O_2'$.

Those reactions, then, tend to take place to completion which result in the formation of a substance that is either insoluble, volatile, or slightly dissociated. It is the chemical changes of this kind which are most frequently employed in analytical chemistry, where it is desirable that the reactions used be so complete with respect to the transformation of at least one substance that the quantity of that substance remaining shall be negligible. As between two such substances having a common component that one will result which removes this component more completely from the sphere of action. Of a number of slightly soluble substances the least soluble will form: $AgCl + KI = AgI + KCl$; $PbSO_4 + H_2S = PbS + H_2SO_4$; these reactions take place rather than the reverse reactions because silver iodide and lead sulphide are less soluble respectively than silver chloride and lead sulphate. There is no difference in principle between these and such changes as: $AgNO_3 + KI = AgI + KNO_3$; $Pb(NO_3)_2 + H_2S = PbS + 2HNO_3$.

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*In this way even a substance but little dissociated may suffer complete precipitation. In a solution of hydrosulphuric acid there is equilibrium between the non dissociated acid and its ions. When a lead salt is added the sulphur ion is taken up to form lead sulphide, which precipitates. To restore equilibrium hydrosulphuric acid dissociates, forming more of the sulphur ion, which in turn unites with the lead ion, necessitating further dissociation of hydrosulphuric acid, and so on until only so little non-dissociated hydrosulphuric acid remains as is in equilibrium with the sulphur ions in a saturated solution of lead sulphide.

17. Solubility.

A solution is a homogeneous mixture of two or more substances. Those with which the analyst has most commonly to deal are mixtures of a solid, sometimes a gas, with a liquid, usually water. When a solid is brought into contact with a solvent it enters the latter by virtue of a force similar to that which enables a gas or vapor to enter a vacuum, and diffusion takes place until the mixture is quite homogeneous and a definite ratio has been established between the concentration of the dissolved substance and the concentration of the solid. Such a solution, in equilibrium with the solid, is a saturated solution. A supersaturated solution contains more of the dissolved substance. If but slightly supersaturated it is perfectly stable so long as the solid is not present, but addition of the minutest particle of the solid causes precipitation (crystallization) and the saturated solution results.

There is infinite variety in the solubility of solids in water, from those which cannot be shown by analytical methods to dissolve at all to those which may be mixed in all proportions with the solvent. All substances must be considered to be soluble to some extent, and when a body is said to be insoluble it is understood to mean that the solubility is so slight as to be for most purposes negligible. The precipitates which are obtained in analytical work are practically insoluble, this designation covering those which dissolve to the extent of 100 milligrams or less in a liter of water. Even here there is wide variety. AgI, a few thousandths of a milligram * of which dissolve in one liter, is something like 600 times less soluble than AgCl; 2.3 milligrams $BaSO_4$ dissolve in one liter; 46 milligrams $PbSO_4$, and so on; in the presence of other substances with which the precipitates have an ion in common, which is usually the case in analysis, even these slight solubilities are lessened.

The substances designated as "sparingly soluble" have for the most part a solubility of one to ten grams per liter (one to ten milligrams per cubic centimeter). These solubilities also are decidedly lessened under the actual conditions of analysis.

18. The Solubility-Product.—A solution becomes saturated and will take up no more of the solid when the concentration of the non-dissociated portion of the dissolved body has reached a certain definite value. Equilibrium then exists between solid and solute (matter in solution). The non-dissociated substance is, furthermore, in equilibrium with the dissociated portion. Silver chloride, for instance, dissociates into $Ag^{\cdot}$ and Cl', and we have the equilibrium equation $[Ag^{\cdot}] \times [Cl'] = k[AgCl]$, the formulas enclosed in brackets standing for the concentrations of the respective substances (see §20). But $[AgCl]$, the concentration of the non-dissociated portion, is constant. Therefore $[Ag^{\cdot}] \times [Cl']$ is constant, that is, the product of the concentrations of the ions of a substance is always the same in its saturated solution at a given temperature. This Ostwald has called the *solubility-product*. A substance with large solubility-product is freely soluble; with small solubility-product but little soluble. So long as the ions are in such slight quantity that the product of their concentrations is less than the solubility-product, the solution will be capable of taking up more of the solute. When the solubility-product is exceeded, as by addition of silver nitrate solution to hydrochloric acid solution, precipitation takes place until the ions are present only in such quantity that the product of their concentrations equals the solubility-product. Precipitation is thus preceded by supersaturation and there remains always a saturated solution of the precipitated substance. If the silver ion is added in large excess to a saturated solution of silver chloride, the solubility-product will be exceeded; equilibrium is established through removal of some of the chlorine ion by precipitation as silver chloride, increase in one of the factors of the solubility-product necessitating a proportionate decrease in the other factor. Silver chloride is less soluble, then, in silver nitrate solution than in water, and in general *the solubility of any substance is lessened by the presence of another substance with which it has an ion in common.* This is the reason for the practice of using an excess of reagent for precipitation.

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* A milligram of powdered solid is, if crystalline, commonly slightly less in bulk than a pinhead; if amorphous, slightly greater. Most precipitates are much bulkier; a milligram of As_2S_3 forms a fairly heavy precipitate in 10 cubic centimeters of water. A pinhead weighs something over ten milligrams, a drop of water fifty milligrams.

Potassium chlorate is precipitated from its saturated solution by the potassium ion of potassium hydroxide or the chlorate ion of sodium chlorate. Barium sulphate solution, formed by bringing together dilute barium hydroxide and sulphuric acid, is precipitated by either barium chloride or sulphuric acid. Silver chloride in its saturated solution is precipitated by silver nitrate or by sodium chloride. Experiment gives quantitative agreement with the theory (Nernst, Z. phys. Chem. 1889, 4, 372; Noyes, Z. phys. Chem. 1890, 6, 241; 1892, 9, 603).

19. On the other hand, any cause which decreases the concentration of either of the factors of the solubility-product, as by taking up a simple ion to form either a more complex ion or a non-dissociated molecule, will cause an increase in solubility, more of the solid dissolving to restore the disturbed equilibrium. Increase of solubility through formation of a slightly dissociated substance is illustrated by the action of an acid on a little-soluble base, as hydrochloric acid on calcium hydroxide. When acid and base are brought together the $H^{\cdot}$ of the acid unites at once with the OH' of the base to form water, which is almost non-dissociated.[*] This lowers $[OH']$ so that the product $[Ca^{\cdot\cdot}] \times [OH']^2$[†] is less than the solubility-product of calcium hydroxide. To re-establish the solubility-product more calcium hydroxide will dissolve, only to have its OH' again taken up by the $H^{\cdot}$ of the acid, and the process repeats itself either until calcium hydroxide has all dissolved and the equilibrium between solid and solute has no longer to be maintained, or until the acid is exhausted and the hydrogen ions are in slight enough concentration to be in equilibrium with the hydroxyl ions of a solution of calcium hydroxide. The solubility in sodium hydroxide of metallic hydroxides, which in such case act as acids, ($Al(OH)_3$, for instance, breaking up slightly into $3H^{\cdot} + AlO_3'''$), is due to precisely the same cause.

Similarly the salt of a weak acid dissolves in a stronger acid. The C_2O_4 ions of calcium oxalate unite with the hydrogen ions of hydrochloric acid to form the slightly dissociated oxalic acid just as the hydroxyl ions of calcium hydroxide unite with hydrogen ions to form water, and in each case more of the solid must dissolve. Calcium oxalate is not dissolved by acetic acid because the latter is even less dissociated than oxalic acid and the hydrogen remains with the non-dissociated acetic acid molecule.

The solubility of iron compounds, as ferrous hydroxide, in potassium cyanide is due to the taking up of the iron into a complex ion. For ferrous hydroxide the solubility-product is $[Fe^{\cdot\cdot}] \times [OH']^2$. The CN' of potassium cyanide reacts with $Fe^{\cdot\cdot}$ to form $Fe(CN)_6''''$: $6CN' + Fe^{\cdot\cdot} = Fe(CN)_6''''$. This removal of $Fe^{\cdot\cdot}$ lowers the product of the ion concentrations below the solubility-product. To restore it more ferrous hydroxide dissolves; $Fe^{\cdot\cdot}$ is again taken up by CN', and the process continues until with excess of potassium cyanide the ferrous hydroxide is completely soluble.

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[*] This is the reason for the fact, long not understood, that the heat given off on neutralization of strong acids by strong bases is the same in all cases, independent of the nature of the acid or base: $Na^{\cdot} + OH' + H^{\cdot} + Cl' = Na^{\cdot} + Cl' + H_2O$. The only reaction that takes place is union of the $H^{\cdot}$ and OH'.

[†] The exponent of the concentration of a substance is fixed by the number of times that substance occurs in the reaction-equation. Here $Ca(OH)_2 = Ca^{\cdot\cdot} + 2OH'$.

The solubility of a salt is in general increased by the presence of another salt with which it has not an ion in common. This influence is in many cases slight.

20. Equilibrium between Substances with a Common Ion.

When two substances with a common ion are brought together not only the solubility but also the extent of dissociation of each is affected. This is particularly observable where one of the two is naturally but slightly dissociated.

In reactions involving dissociation, the breaking up of a substance into simpler components, the ordinary equilibrium conditions obtain, expressed by the equation $ab = kc$ or $\frac{ab}{c} = k$, in which a and b are the concentrations of the components, c that of the non-dissociated substance, and k the "dissociation-constant." Gaseous NH_4Cl breaks up on heating into NH_3 and HCl. For equilibrium we have: $[NH_3] \times [HCl] = k[NH_4Cl]$. It is evident that if either a or b is increased the other will decrease and c must increase. The quantity of non-dissociated substance (NH_4Cl) is increased by adding either of the products of the dissociation (NH_3 or HCl).

The conditions in the case of electrolytic dissociation are identical. Ammonium hydroxide dissociates into $NH_4^{\cdot}$ and OH' and for equilibrium $[NH_4^{\cdot}] \times [OH'] = k[NH_4OH]$. The introduction of NH_4 ions or OH ions in excess will decrease the dissociation of NH_4OH. NH_4Cl added to NH_4OH thus lowers the concentration of the OH ions and in so doing weakens the power of the base, which is in direct proportion to the OH ion concentration. Addition of fixed alkali hydroxide also increases the quantity of non-dissociated NH_4OH, and facilitates complete expulsion of ammonia by heating. This influence is very marked in the case of a substance whose dissociation is slight, but is scarcely perceptible where the dissociation is from the beginning practically complete. NH_4OH, as a slightly dissociated substance, is present in N/10 solution to perhaps 1½ per cent in the ionic condition. $[NH_4{}^{\cdot}]$ is then 0.0015. $[OH']$ has the same value. Now suppose that to N/10 NH_4OH enough NH_4Cl be added so that it also is N/10 (53.5 grams per liter). NH_4Cl may be taken as 90 per cent dissociated. $[NH_4{}^{\cdot}]$ due to NH_4Cl is then 0.09. This added to 0.0015, the original $[NH_4{}^{\cdot}]$, gives 0.0915, about sixty times the first value, and for the preservation of equilibrium $[OH']$ must decrease in about the same ratio, depriving the solution of its basic power to just that extent.

In a similar manner a neutral acetate, as $NaC_2H_3O_2$, weakens acetic acid by driving back its dissociation and in general a weak acid or weak base is still further weakened by the presence of its neutral salt. This does not hold for strong acids and bases; in fact strong acids, for reasons not clearly understood, are made slightly more active by the presence of their salts.

21. Hydrolysis.

Water, present in most analytical operations, does more than act as a solvent. Acids and bases are active only in the presence of water, as ionization scarcely takes place without it. Anhydrous acids are lacking absolutely in acid properties. Salts also are capable of reaction only in so far as they are dissociated into ions. And owing to the fact that it is itself an electrolyte, containing H and OH ions in slight quantity, water effects a further change in many salts. The equilibrium obtains $[H^{\cdot}] \times [OH'] = k[H_2O]$. The concentration of non-dissociated water varies so little and is so large in proportion to that of other substances present that it may be regarded as constant. *The product of the concentrations of $H^{\cdot}$ and OH' is, then, practically the same in all water solutions.* If one is increased the other must decrease in just the same proportion.

Now, if the salt of a weak acid, as Na_2CO_3, be dissolved in water, the hydrogen ions, few though they are, are too many to be in equilibrium with the concentrated CO_3 ions of the Na_2CO_3, for wherever $H^{\cdot}$ and CO_3'' are in solution together they must, as the ions of a very weak acid, for the most part unite to form non-dissociated H_2CO_3. The matter is adjusted by the following reactions: $2H^{\cdot} + 2OH' + CO_3'' + 2Na^{\cdot} = H_2CO_3 + 2Na^{\cdot} + 2OH'$, and $2Na^{\cdot} + CO_3'' + 2H_2O = H_2CO_3 + 2OH' + 2Na^{\cdot}$. The salt of a weak acid in water solution thus takes on alkaline reaction, due to the OH', with formation of the non-dissociated acid, which if insoluble may precipitate ($Zn(OH)_2$ from Na_2ZnO_2, etc.). In some cases the non-dissociated acid may be detected in the solution by its odor (KCN, $NaC_2H_3O_2$).

In a precisely similar manner the salt of a weak base takes on acid reaction owing to the formation of the non-dissociated base. The latter is sometimes precipitated in the process (salts of Bi, Sb, Sn, Hg, etc.) and sometimes remains in solution as a colloid (ferric salts, etc.).

This action of water, splitting up the salt of a weak acid or base to form again in whole or in part the acid and base, is called hydrolysis.

Hydrolysis of the salt of a weak acid is hindered by the presence of OH', which decreases the $H^{\cdot}$ concentration; and similarly the salts of weak bases are more stable in the presence of $H^{\cdot}$, which decreases the quantity of OH'. Na_3AlO_3 and like compounds are soluble without decomposition only in excess of alkali hydroxide, while salts of Bi, Sn, Sb and other insoluble weak bases require the presence of an acid to hold them in solution.

22. The Periodic System of the Elements.

Taking the elements as arranged in the table (§23) showing the periodic system, there is in general (not always) increase in positive or base-forming characteristics with increase in atomic weight in the vertical column. There is a similar gradation in the horizontal row, the positive qualities here decreasing with increasing atomic weight.

When a metal is immersed in a solution of its salt the solution takes on a positive or negative charge of electricity according as the tendency is greater for the metal to go into solution (as a positive ion) or for the dissolved metal (the kathion) to separate out in the free state. That metal is most positive electrically which develops the greatest positive difference of potential * in a solution containing its ions in definite concentration. This difference of potential is a measure of the tendency of the metal to go over into the ionic form, that is, of the readiness with which it is oxidized, or with which it acts as a reducing agent. The metals arranged according to the magnitude of the difference of potential which they thus cause give the voltaic series (§27).

With this positive electrical character is associated, as a rule, strength of the hydroxide as a base, carrying with it ability to form with strong acids salts which are not hydrolyzed by water and not broken up by heat.

A non-metal, similarly, causes in a solution containing its ions a negative charge which is a measure of the non-metallic character of the element in question, its ability to form strong acids, its strength as an oxidizing agent, etc.

The hydroxides of the elements in the second horizontal row, beginning with sodium, afford an interesting comparison. Sodium hydroxide is one of the strongest bases; magnesium hydroxide is a base of medium strength and its salts even with strong acids exhibit a tendency to hydrolysis; magnesium chloride above ordinary temperature can be broken up by water into magnesium oxide and hydrochloric acid. Aluminum hydroxide is a weak base, its salts, as $AlCl_3$, hydrolyzing with water, giving their solution acid reaction. Aluminum hydroxide acts also as a feeble acid

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* The difference of potential between electrode and solution is called positive when the solution takes on a positive charge; negative when the solution takes on a negative charge.

whose salts, as Na_3AlO_3, unless in the presence of excess of hydroxyl ion (fixed alkali hydroxide) are decomposed by water into NaOH and $Al(OH)_3$, which is precipitated. The hydroxide of silicon is weakly acid and more weakly basic; Na_2SiO_3 is largely hydrolyzed, while $SiCl_4$ is completely decomposed by water. In the hydroxides of phosphorus the acid properties are decidedly stronger than the basic. The general rule that an element in a higher valence has more pronounced acid-forming tendencies than the same element in a lower valence holds in the case of phosphorus, phosphoric acid, H_3PO_4 ($P(OH)_5 - H_2O$) being stronger than phosphorous acid, H_3PO_3 ($P(OH)_3$). Sulphur in its valence of six forms a strong acid, H_2SO_4 ($S(OH)_6 - 2H_2O$), in its valence of four a weaker acid, sulphurous, H_2SO_3 ($S(OH)_4 - H_2O$); its basic properties have practically disappeared. With chlorine the acid-forming tendency reaches its maximum; perchloric acid, $HClO_4$ ($Cl(OH)_7 - 3H_2O$), and chloric acid, $HClO_3$ ($Cl(OH)_5 - 2H_2O$), are among the strongest acids known.

There is a similar gradation in other horizontal rows from base-forming to acid-forming elements.

In the vertical columns, each containing a group of elements more or less closely related to one another, there is a general tendency to increase in positive character with increasing atomic weight. This tendency is marked in the case of the alkali metals, the ease of oxidation, shown in the readiness with which the metal decomposes water, and correspondingly the difficulty of reduction, increasing from lithium to caesium.

In the next column, that containing the alkaline earth metals, all less strongly basic than the alkali metals, there is increase in basic power from beryllium to barium, the latter ranking near the alkali metals in its strength. The carbonates are decomposed by heat with increasing difficulty, and there is less tendency to hydrolysis of the chlorides and similar salts, as the atomic weight increases.

In the following column, the hydroxides of boron are weak acids, that of aluminum is more basic, while thallium, the element with highest atomic weight, is a decided metal.

The next column begins with carbon, whose oxide, CO_2, forms a weak acid. The hydroxides of silicon are weaker acids and stronger bases. Tin and lead are basic elements, but their hydroxides still retain weakly acid properties and dissolve in fixed alkali hydroxide.

In the nitrogen family nitrogen itself forms a strong acid; in phosphorus also the acid properties preponderate; in arsenic they are less decided, while antimony is primarily a basic metal, although its hydroxides still dissolve as weak acids in fixed alkali hydroxide. In bismuth, which is weakly basic, the acid characteristics fail entirely.*

Sulphur, selenium, and tellurium in the next column constitute a similar series, all forming acids as H_2SO_4, H_2SeO_4, H_2TeO_4, which are weaker the higher the atomic weight of their characteristic element. From oxygen to tellurium there is an augmentation of positive characteristics, tellurium having many of the properties of a metal. There is a corresponding decrease in negative strength, and oxygen replaces sulphur from H_2S (imperfect combustion in air) just as a halogen of lower atomic weight replaces one of higher atomic weight from its hydracid.

In the halogen family we find decrease in the stability of hydracids and their salts with increasing atomic weight, decrease in the strength of the halogen as an oxidizer, and increase in the efficacy of the hydracid (the ion) as a reducing agent. Each halogen has a greater tendency to enter the ionic state than the others with higher atomic weight, and those with lower atomic weight therefore displace those of higher atomic weight from the hydracids and their salts.

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* See the Qualitative Chemical Analysis of Prescott and Johnson, Fifth Edition, 1901, page 7.

23. Metals of the Silver and Tin and Copper Groups in the Periodic System.

Li 7	Be 9.1	B 11	C 12	N 14	O 16	F 19	
Na 23	Mg 24.4	Al 27	Si 28.4	P 31	S 32	Cl 35.5	
K 39.1	Ca 40	Sc 44	Ti 48	**V** 51	Cr 52	Mn 55	**Fe 56, Co 59, Ni 58.7**
Cu 63.6	Zn 65.4	Ga 70	**Ge** 72	**As** 75	**Se** 79	Br 80	
Rb 85.4	Sr 87.6	Y 89	Zr 90.6	Cb 94	**Mo** 96		**Ru** 102, **Rh** 103, **Pd** 106
Ag 108	**Cd** 112	In 114	**Sn** 118.5	**Sb** 120	**Te** 127	I 126.9	
Cs 133	Ba 137.4	La 138 etc.					
		Yb 173		Ta 183	**W** 184		**Os** 191, **Ir** 193, **Pt** 195
Au 197	**Hg** 200	Tl 204	**Pb** 207	**Bi** 208			
			Th 232		**U** 240		

THE METALS.

The Silver and Tin and Copper Groups.

24. Group I.—Metals forming insoluble chlorides: Ag, Pb, Hg (monovalent).

Group II.—Metals (not belonging to Group I.) whose sulphides are insoluble in dilute acid: Sn, As, Sb, Hg (divalent), Pb,* Bi, Cu, Cd, and of less common occurrence Au, Ge, V, Mo, W, Se, Te, Ru, Rh, Pd, Os, Ir, Pt.

These metals are at the negative end of the voltaic series. Their tendency to go over from the metallic to the ionic state is but slight and oxidizing acids (nitric or nitro-hydrochloric) are required to dissolve them. They form weak bases and readily hydrolyzed salts having for the most part acid reaction in water solution. The "noble metals," not readily oxidized or tarnished, and easily reduced from their compounds, are in these groups.

The metals of the Tin and Copper Group may be precipitated as sulphides from dilute acid solution, this being the means of their separation from metals of following groups. The line of division between the groups is fixed by convenience only; strong concentrated acid hinders the precipitation of these sulphides by H_2S, while on the other hand Zinc-Group sulphides are precipitated more or less completely in the presence of very dilute acid. CdS, the most soluble Second-Group sulphide, is completely precipitated in presence of N/2 HCl, and it is of the utmost importance that the solution be not more strongly acid than this when precipitation of the Tin and Copper Group takes place.

The metals of the Tin Subgroup are distinguished from those of the Copper Subgroup by the solubility of the sulphides of the former in ammonium polysulphide with formation of sulpho-compounds (ammonium salts in which sulphur has replaced oxygen).

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* Pb occurs in both groups owing to the decided solubility of its chloride in water and its consequent incomplete precipitation in the Silver Group.

Silver.

25. Metallic silver is used mostly alloyed with a small proportion of copper for hardening; U. S. silver coins contain 10 per cent copper. Plated ware is coated by electrolysis. "Oxidized" silver has a surface of Ag_2S. Lunar caustic is $AgNO_3$, used in solution as indelible ink. AgCl is used for sensitive paper, AgBr for dry plates, and AgI for the sensitive coating of wet plates in photography.

The most important source of silver is galena, PbS, which contains a small proportion of Ag_2S; it is also found native, and as argentite, Ag_2S; pyrargyrite and stephanite, Ag_2S with Sb_2S_3; and cerargyrite or horn silver, AgCl.

Silver forms monovalent ions. Most of its salts are insoluble in water but soluble in NH_4OH.[*]

26. Solutions of silver salts, containing the ion $Ag^{\cdot}$, give precipitates when mixed with other solutions as follows:[†]

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[*] As has already been stated, any cause which takes up the ions of a substance will increase the solubility of that substance. NH_4OH added to a saturated solution of silver salt, as AgCl, in contact with the solid takes up $Ag^{\cdot}$ to form a complex ion. This lowers $[Ag^{\cdot}] \times [Cl']$ (symbols in brackets denote concentration of the substances), below the solubility-product, and solid AgCl dissolves to restore it. NH_4OH at once combines with the freshly-formed $Ag^{\cdot}$ and so the process continues until either NH_4OH or AgCl is exhausted. Some salts, as AgI, dissolve but little in NH_4OH because the $Ag^{\cdot}$ from the dissociation of the trace of the complex formed (complex ions always break up to some extent into their components) is in great enough concentration to satisfy the very small solubility-product of AgI.

[†] The student should obtain these reactions with a salt of silver before testing for silver in mixtures of unknown composition. In each case the chemical equation should be written showing as fully as possible the change that has taken place. It is far better to do this while working at the table, or at all events before going on with other substances. The writing of the equation throws light upon the management of the test and corrects mistakes in manipulating. Taking the $Ag^{\cdot}$ precipitates:

$AgNO_3$ with HCl gives a precipitate.

To ascertain what the precipitate contains, and in what proportion, the student must either himself subject it to a quantitative analysis or accept the statement of some one else who has done so. The composition is never to be assumed on theory. Consulting a text-book we have:

$AgNO_3 + HCl = AgCl + ----$

When **hydrosulphuric acid** or a s
to a silver salt solution the solubili
phide, $[Ag^{\cdot}]^2 \times [S'']$, is exceeded a
a black precipitate, reducing the con
and sulphur ions until they are pr
quantity to give the solubility-prod
soluble in hot dilute HNO_3, insoluble

Solution of **hydrochloric acid** or of
the **chlorine ion,** which forms with
chloride, insoluble in water. Hydroc
chlorides added to a solution of a sil
cipitate AgCl, white, becoming drab
mation of a compound containing les
soluble in NH_4OH to $Ag(NH_3)_2Cl$*;
soluble in strong HCl.

Similarly a solution of **hydrobromic**
contains the **bromine ion** and precipi
AgBr, slightly yellowish, insoluble in
in NH_4OH.

Hydriodic acid and **soluble iodides** ha

And we know, or ascertain, that the H and NO_3 re
AgCl is precipitated constitute a solution of the
NO_3 ion.)
Similarly—

precipitate silver iodide, AgI, yellowish, soluble in KI or NaI, insoluble in HNO_3, insoluble in NH_4OH.

Cyanides (CN′) precipitate AgCN, white, soluble in excess to $KAg(CN)_2$ (ions $K^{\cdot}$ and $Ag(CN)_2'$); insoluble in HNO_3.

Phosphates, carbonates, chromates, oxalates, arsenates and **arsenites** precipitate the corresponding silver salts, soluble in HNO_3 and also in NH_4OH.

27. The metals may be so arranged in order that each will be precipitated in metallic form from solution by those which precede it and will precipitate those which follow it. This is the so-called *voltaic series*. It is as follows: K, Na (Ba, Sr, Ca), Mg, Al, Mn, Zn, Cd, Fe, Co, Ni, Sn, Pb, H, Bi, Sb, As, Cu, Hg, Ag, Pd, Pt, Au. The metals first named are the positive metals, stable in combination; the last of the series are the easily reduced negative or noble metals. Of the metals in this list all but three will precipitate silver from its solutions, while silver throws down the metal from solutions of Pd, Pt, or Au. A bright strip of **copper**, for example, in solution of $AgNO_3$, becomes coated with metallic silver, lustrous on drying and gently rubbing, while cupric ions enter the solution.

Reducing agents * in general readily form metallic silver from compounds of the element. $Fe^{\cdot\cdot}$ throws it down as a brown-black precipitate, and is oxidized to $Fe^{\cdot\cdot\cdot}$. A silver mirror lining may be made in a test-tube or flask by treating

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* A reaction causing a change in the number of equivalents of substance with which an element is united involves oxidation and reduction. An element is said to be reduced when it is freed from combination with a non-metallic (negative) element or group, or caused to enter into combination with a metallic (positive) element or group. The change of $HgCl_2$ to HgCl or Hg, or of free Cl to HCl is a reduction, of the Hg in the first case and of the Cl in the second. The reverse process, addition of a negative or removal of a positive element or group, is oxidation. Sn is oxidized when $SnCl_2$ changes to $SnCl_4$; S is oxidized when it is liberated in the free state from H_2S. Oxidation and reduction always accompany each other, the oxidizing agent being reduced and the reducing agent oxidized.

An ion is oxidized when it increases its positive or diminishes its negative charge of electricity; reduced when the negative charge is increased or the positive decreased. See Ostwald, Grundlinien der anorganischen Chemie, p. 575; and Grundriss der allgemeinen Chemie, 3d edition, pp. 398 and 439.

pipe silver compounds give globul
$4AgCl + C + 2Na_2CO_3 = 4Ag + 4$

Lead.

29. Common forms: Metallic lead shot, solder, type-metal, etc. White le litharge or massicot is PbO, added to o used in glass-making, etc.; red lead is is $PbCrO_4$; sugar of lead is the acetate In the common storage battery the pos negative a composition containing lead

Mineralogy: Galena, PbS; cerussit $PbSO_4$; pyromorphite, $Pb_3(PO_4)_2.PbCl$

30. The metal is dissolved by dilu HCl, H_2SO_4, or strong HNO_3. It di tilled water. Lead pipes which con used for drinking soon become lined w ing, a mixture of oxide and carbonate.

31. Lead salts in solution contain t precipitates as follows:

Fixed alkali hydroxide (the **hydrox** concentration) forms lead hydroxide, P acts as a weak acid and gives with hydroxide a soluble salt, as Na_2PbO

in **ammonium** hydroxide is prevented by hydrolysis, ammonium hydroxide being a much weaker base than the fixed alkali hydroxides.

Solutions of **carbonates,** as Na_2CO_3, contain **hydroxyl ion** as well as **carbonate ion,** owing to partial hydrolysis, and the precipitate which they cause in solution of a lead salt is a mixture of hydroxide and carbonate, white. Carbonic acid (H_2CO_3) is but little dissociated into its ions, being a very weak acid, and it causes no precipitation.

Hydrosulphuric acid and soluble **sulphides** (the **ion S''**) precipitate lead sulphide, PbS, black, insoluble in dilute acids or in alkalis; a delicate test for lead (1-100,000). In the presence of concentrated HCl the precipitate is brick-red.

Sulphuric acid and soluble **sulphates** (the **ion SO_4''**) precipitate lead sulphate, $PbSO_4$, white, slightly soluble in strong acids; it is soluble in $NaOH$ (in common with all the lead salts here mentioned except the sulphide), a useful distinction from $BaSO_4$.

Hydrochloric acid and soluble **chlorides** (the **ion Cl'**) precipitate lead chloride, $PbCl_2$, white, soluble 10 grams per liter cold, separated from $AgCl$ and $HgCl$ by its solubility in hot water; it is less soluble in dilute HCl than in water (§18).

Hydrobromic acid and soluble **bromides** (the **ion Br'**) precipitate lead bromide, $PbBr_2$, white, soluble 6 grams per liter.

Hydriodic acid and soluble **iodides** (the **ion I'**) precipitate lead iodide, PbI_2, yellow, soluble 0.6 gram per liter, somewhat soluble in excess; this precipitate, heated with considerable water, recrystallizes in characteristic golden flakes.

The **chromate ion, CrO_4''**, of K_2CrO_4 precipitates lead chromate, $PbCrO_4$, yellow; $K_2Cr_2O_7$ solution contains CrO_4 ions and gives the same precipitate.

The **phosphate ion, PO_4'''**, of soluble **phosphates** precipitates lead phosphate, $Pb_3(PO_4)_2$, white, insoluble in dilute acetic acid.

Oxalates precipitate PbC_2O_4, white; **sulphites** $PbSO_3$, white.

32. Heated on **charcoal** with Na_2CO_3 lead compounds give globules of the metal, soft and malleable (distinction from bismuth), a yellow crust of PbO forming around the mass: $2PbSO_4 + 2Na_2CO_3 + C = 2Pb + 2Na_2SO_4 + 3CO_2$. The sulphate suffers reduction at the same time: $Na_2SO_4 + 2C = Na_2S + 2CO_2$. Heated with $\mathbf{Na_2CO_3}$ alone transposition takes place, owing probably to the greater solubility of $PbSO_4$ in the fused mass: $PbSO_4 + Na_2CO_3 = Na_2SO_4 + PbO + CO_2$. See further under H_2SO_4. This fusion is used in analysis for obtaining the substance in a soluble form. The fused mass is treated with water and the resulting solution tested for the acid ion (SO_4''), while the residue is dissolved by HNO_3 and this solution tested for the Pb ion.

Mercury.

33. Mercury, or quicksilver, is used in the liquid form for scientific instruments. Finely divided as a gray powder it is used in medicine, as in blue mass and blue pill. Calomel is mercurous chloride, HgCl; corrosive sublimate, mercuric chloride, "bichloride of mercury," $HgCl_2$. Mercury is found native and as cinnabar, HgS.

34. Mercury is dissolved by HNO_3, a monovalent (mercurous) or divalent (mercuric) ion forming according as mercury or acid is in excess. Both are ions of weak bases and the soluble salts are split up by water with precipitation of basic compounds, the solution taking on acid reaction; acidulated water is required to prevent this precipitation. $Hg^{\cdot}$ is oxidized to $Hg^{\cdot\cdot}$ by oxidizing agents, as HNO_3, Cl, etc., and $Hg^{\cdot\cdot}$ is reduced to $Hg^{\cdot}$ by metallic mercury and other reducing agents.

35. Solutions of **mercurous** compounds, containing the **ion** $\mathbf{Hg^{\cdot}}$, give precipitates as follows:

Fixed alkali hydroxide (the **hydroxyl ion**) forms Hg_2O, black.

Ammonium hydroxide causes the formation of a complex compound in which divalent Hg replaces H in ammonium salt, while black metallic mercury is liberated: $2HgNO_3 + 2NH_4OH = NH_2HgNO_3 + NH_4NO_3 + Hg + 2H_2O$.

Hydrosulphuric acid and soluble **sulphides** (the **sulphur ion**) precipitate Hg_2S, stable only at low temperatures, breaking up into HgS and Hg.

The **chlorine ion,** as contained in dissolved **chlorides** and **hydrochloric acid,** precipitates HgCl, white, precipitated with the Silver Group, blackened by NH_4OH owing to separation of Hg.

Hydrobromic acid or a soluble **bromide** (the **bromine ion**) precipitates HgBr, yellowish white.

Hydriodic acid or a soluble **iodide** (the **iodine ion**) precipitates HgI, greenish, breaking up into HgI_2 and Hg.

Carbonate solutions, containing the **carbonate ion, CO_3''**, precipitate Hg_2CO_3 cold, a basic carbonate hot.

36. Mercuric salts, with the **ion $Hg^{\cdot\cdot}$**, are precipitated from solution as follows:

Fixed alkali hydroxide gives HgO, "red precipitate," red to yellow, the difference in color being due to the finer state of division of the latter.

NH_4OH precipitates NH_2HgCl, "white precipitate," somewhat soluble in excess.

The **sulphur ion,** as in **hydrosulphuric acid** and soluble **sulphides,** precipitates HgS, black; white to yellow and brown when the reagent is not in excess. When heated, or on digestion with alkali sulphides, it goes over into the more stable red crystalline form (vermilion, used as a pigment). HgS is soluble in nitro-hydrochloric acid, not in HNO_3 or HCl; soluble in K_2S, not in $(NH_4)_2S$.

Hydriodic acid or a soluble **iodide** (the **iodine ion**) precipitates HgI_2, yellow to red, soluble in excess of KI, forming K_2HgI_4 (and other complex compounds), used as a reagent (Nessler's) for detecting ammonia, also as a general precipitant of alkaloids.

completely precipitated as the oxide
presence of chlorides the dissociatio
so slight that precipitation will not
the other hand NaCl solution reacts
it gives opportunity for the formatio
ciated $HgCl_2$, and an alkaline solu
$2NaCl + H_2O = HgCl_2 + 2NaOH$.

38. With either mercurous or merc
tion precipitates at first HgCl, white
$2HgCl_2 + SnCl_2 = 2HgCl + SnCl$
$2Hg + SnCl_4$; $HgCl_2 + SnCl_2 = Hg$
lic precipitate, warmed with HCl an
rod, unites in globules of mercury.
in solution of any mercury compound
mercury, silver-white when dried and

39. With **heat** all forms of mercury
compounds of mercury, heated dry v
give mercury carbonate, which decom
of metallic mercury on the cool part
oxides and most other compounds gi
alone, but the halogen compounds re
an alkali, otherwise they sublime un
$Na_2CO_3 = Hg + O + 2NaCl + CO_2$

a mordant in dyeing, is $SnCl_2, 2H_2O$; also used as a reducing agent in chemical manufacture; butter of tin, $SnCl_4$, and pink salt, $(NH_4)_2SnCl_6$, are also used by dyers; mosaic gold is SnS_2. Tin occurs in nature as cassiterite or tin-stone, impure stannic oxide, SnO_2.

41. Tin dissolves in hot HCl or very dilute HNO_3 as the stannous ion, $Sn^{\cdot\cdot}$, in nitro-hydrochloric as a tetravalent compound. It forms also, on dissolving $Sn(OH)_2$ and $Sn(OH)_4$ in alkali hydroxides, the anions SnO_2'' and SnO_3'' respectively. Hydrolysis of the salts of these anions, that is, the tendency of the $H^{\cdot}$ of the water to unite with the anion to form the non-dissociated acids H_2SnO_2 and H_2SnO_3, which are insoluble, is counteracted by OH', which reduces the $H^{\cdot}$ concentration, to which hydrolysis is due (see §21). The salts of these, as of other very weak acids, are therefore stable in solution only in the presence of excess of alkali hydroxide. All the metallic hydroxides which dissolve in excess of fixed alkali hydroxide furnish examples of this.

Salts of $Sn^{\cdot\cdot}$ undergo hydrolysis in contact with water and require the addition of acid to hold them dissolved. Dilution with water causes precipitation of the white Sn_2OCl_2, stannous oxychloride. Solution of $SnCl_4$ contains the tin almost wholly as stannic hydroxide or stannic acid, precipitated by neutralizing with NaOH.

42. **Alkali hydroxides** precipitate from solutions of stannous salts white stannous hydroxide, $Sn(OH)_2$, which is capable of acting feebly both as acid and as base; it dissolves in excess of fixed alkali hydroxide, soluble alkali stannite, as Na_2SnO_2, forming. Hydrolysis prevents the formation of a soluble stannite from $Sn(OH)_2$ and the weaker base, NH_4OH.

Dissolved **carbonates** precipitate $Sn^{\cdot\cdot}$ as the hydroxide, hydrolysis being practically complete.

Hydrosulphuric acid and soluble **sulphides**, containing the **sulphur ion**, precipitate from stannous solutions SnS, brown (SnS_2 is yellow). The precipitate dissolves in yellow **ammonium (poly)sulphide** (not easily in colorless ammonium generator with HCl and test the solu or white precipitate (Hg or HgCl) presence of stannous salt.

44. Stannous salts go over easily are ready **reducing agents. Mercu** **silver** compounds (**$Ag^{\cdot}$**), **ferric** compo and even the **oxygen** of the air will good test for tin based on this prop KOH in excess to the solution, which other metals, filter, and treat *cold* w solution (1 vol. N/4 $AgNO_3$ to 15 vo present a black precipitate of metallic $Sb^{\cdots}$ and $As^{\cdots}$ are likely to give the s Tetravalent tin must be reduced by A tin redissolved in HCl before adding

45. Heated on **charcoal** with Na_2C tin is easily reduced from its compound globules, a slight white incrustation

Arsenic.

46. Common forms: Arsenous oxide, Fowler's solution, 1 per cent As_2O_3 in green and Schweinfurth being AsO_3''' * and AsO_4''', respectively. $As^{\cdot\cdot\cdot}$ and $As^{\cdot\cdot\cdot\cdot\cdot}$ are also present, indicated in the former case by the fact that acid increases the sparing solubility of the oxide, and in both cases by the capability of precipitation as sulphide.

48. **NH_4OH, KOH**, and **Na_2CO_3** do not precipitate As from its solutions.

Solutions of **arsenous** compounds with **H_2S** form As_2S_3, remaining dissolved in the colloid † form unless a neutral salt or an acid be present. Delicacy 0.1 mg. As per cc. Alkali prevents the precipitation owing to the formation of soluble sulpho-compounds. The precipitate is almost insoluble in HCl, is dissolved by chlorine (nitro-hydrochloric acid or $KClO_3 + HCl$), forming H_3AsO_4, and dissolves in ammonium sulphide (distinction from Copper-Group metals); also in ammonium carbonate (distinction from Sb and Sn): $2H_3AsO_3 + 3H_2S = As_2S_3 + 6H_2O$; $As_2S_3 + 10Cl + 8H_2O = 2H_3AsO_4 + 3S + 10HCl$; $As_2S_3 + 3(NH_4)_2S = 2(NH_4)_3AsS_3$.

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* The precipitates, as Ag_3AsO_3, formed on addition of metallic ions to the solution correspond in composition to the ion AsO_3''', and H_3AsO_3 or $H_6As_2O_6$ is therefore present in the solution, but it may be only in very small quantity. Which of the various acids ($H_6As_2O_6$, $H_4As_2O_5$, $H_2As_2O_4$, etc.) capable of formation by the union of arsenous oxide and water, actually preponderates in the solution is not known. Equilibrium obtains among them, requiring a certain concentration of each. Addition of excess of $Ag^{\cdot}$ takes out that ion with which $Ag^{\cdot}$ forms the least soluble compound; the acids present readjust themselves, forming more of the ion removed, in order to restore the equilibrium. This is again precipitated by the $Ag^{\cdot}$, and so the process continues until practically all the arsenic present has been transformed into the precipitated ion and removed in that way, the changes taking place almost instantaneously. Precipitation of arsenic almost completely as Ag_3AsO_3 therefore does not show that the arsenic was present to that extent as H_3AsO_3. The composition of a precipitate (and the same is true of crystals obtained by evaporation) cannot be taken as evidence of the composition of the solution. That substance separates in either case which is least soluble, and is further formed at the expense of other dissolved substances.

† The colloids (the word means glue-like), so called in distinction from the crystalloids, which have a well-defined solid form, are a class of gelatinous substances which have no fixed solubility in water. Their solutions are unlike solutions of other substances in some important particulars, and stand halfway between the true solution and the mechanical suspension or emulsion. They are as a rule precipitated by addition of an acid or a salt. Albumen, starch, the metallic sulphides, silica, and the hydroxides of iron and aluminum are some of the substances that may take on the colloid form.

poisoning.

$AsCl_3$ volatilizes on heating strong H
ous compounds.

49. Arsenic acid, H_3AsO_4, forms salts
phates in solubilities and in appearan
precipitates from H_3AsO_4 solution As_2
full precipitation requiring several hour
gas in warm solution. Little or no
first (distinction from arsenous compou
cipitation reduce with H_2SO_3, boil off
pass in H_2S. The solubilities of As_2
As_2S_3.

Magnesium salts (**$Mg^{\cdot\cdot}$**), in the pre
salts (the **ammonium ion**) and N
$MgNH_4AsO_4$, white (distinction from
silver salts, containing the **ion $Ag^{\cdot}$**, p
reddish. **Ammonium molybdate** precipi
nium arsenomolybdate, resembling the

50. Hydrogen generated in the prese
pounds forms gaseous arsine or arse
AsH_3,* easily decomposed by heat with d
As, this reaction constituting **Marsh's**
tecting as little as 0.001 mg. As. Obta
hydrogen by treating granulated zinc w

in the $AgNO_3$, showing that arsenic is not present as an impurity in the materials used, introduce into the flask the solution under investigation, which must be free from oxidizing agents, sulphides, or organic matter.* If arsenic is present a **mirror** of metallic arsenic will deposit in the tube beyond the flame (a) (antimony deposits both sides of the flame), while arsine escaping decomposition here will cause a black deposit of metallic silver in the $AgNO_3$ solution (b) (SbH_3 causes precipitation of black Ag_3Sb). When all the air has been expelled from the apparatus the tube may be withdrawn from the $AgNO_3$ solution, or disconnected and the escaping gas ignited. As_2O_3 and water are formed. If now complete combustion be prevented by holding a cold object, as a piece of porcelain, in the flame, the **spot** of steel-gray metallic arsenic (antimony velvety black) will deposit as soot (c). The spots of arsenic are soluble, antimony spots insoluble, in solution of sodium hypochlorite.

(a) $2AsH_3$ heated $= 2As + 3H_2$
(b) $AsH_3 + 6AgNO_3 + 3H_2O = 6Ag + H_3AsO_3 + 6HNO_3$
(c) $4AsH_3 + 3O_2 = 4As + 6H_2O$

Passing the gaseous hydrides into $AgNO_3$ solution separates As from Sb, the latter going almost wholly into the precipitate. To show the presence of As in the solution filter off the precipitate, remove excess of silver (the silver ion) by $CaCl_2$, and pass H_2S, giving yellow As_2S_3.

$$H_3AsO_3 + 3Zn + 3H_2SO_4 = AsH_3 + 3ZnSO_4 + 3H_2O$$
$$H_3AsO_4 + 4Zn + 4H_2SO_4 = AsH_3 + 4ZnSO_4 + 4H_2O$$

51. Metallic **aluminum** and strong solution of potassium or sodium hydroxide with arsenic compounds on boiling give AsH_3, a distinction and separation from Sb. Phosphoric acid interferes, giving PH_3. The sulphide of arsenic may be used in this test.

52. Arsenous compounds are oxidized to arsenic compounds, as As_2O_5 or H_3AsO_4, by $\mathbf{HNO_3}$, **Cl**, **Br**, $\mathbf{KMnO_4}$, and a large number of **oxidizing agents.** **H_2SO_3, thiosulphates, $H_2C_2O_4$, stannous** compounds (the **ion $Sn^{\cdot\cdot}$**), and other **reducing agents** change arsenic compounds to arsenous.

---

* Organic matter may be destroyed by HCl and $KClO_3$ or by HNO_3.

Copper foil placed in a solution acidulated with HCl and warmed becomes coated with iron-gray copper arsenide, Cu_5As_2 (Reinsch's test). Delicacy ca. 0.01 mg. As in 5cc.*

53. All compounds of As, heated with Na_2CO_3 on **charcoal,** give a garlic odor. Dried arsenical material with a fragment of charcoal pressed down on it, in a small tube closed at one end, gives on heating first the charcoal and then the arsenical matter a mirror of As above the heated part, and the garlic odor is obtained. As_2O_3 heated alone sublimes unchanged, forming microscopic octahedral crystals.

Antimony.

54. Common forms: Metallic antimony in certain alloys; type-metal contains Pb, Sb and Sn; britannia-metal, Sn, Sb and Cu. Butter of antimony is $SbCl_3$; stibnite, Sb_2S_3, a black mineral resembling graphite, "black antimony"; liver of antimony, K_3SbS_3; Kermes mineral, Sb_2O_3 and Sb_2S_3; crocus of antimony, $\frac{4}{5}$ Sb_2O_3 and $\frac{1}{5}$ Sb_2S_3; golden sulphide, Sb_2S_5; James' powder, 1 part Sb_2O_3, 2 parts $Ca_3(PO_4)_2$; tartar emetic, potassium antimonous tartrate, $KSbOC_4H_4O_6$.

55. Antimony forms an antimonous and a very weak antimonic kathion with valence of three and five respectively, also the monovalent anions SbO_2' and SbO_3' stable only in the presence of OH ions; also complex ions with tartaric and other acids. Antimony salts in water undergo hydrolysis, the OH' of the water combining with $Sb^{\cdot\cdot\cdot}$ and precipitating as basic salt. The addition of $H^{\cdot}$ in the form of any strong acid prevents this by decreasing the concentration of OH'. See §**21**. The solution in acidulated water is precipitated on dilution, in the presence of HCl as white SbOCl, soluble in tartaric acid owing to the formation of a complex ion (distinction from Bi and Sn). See §**18.**

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* Further upon special reactions of arsenic as applied in the detection of poisons see the Qualitative Chemical Analysis of Prescott and Johnson, fifth edition, 1901, pages 62 to 70.

56. Antimonous salts in solution contain the ion $Sb^{\cdot\cdot\cdot}$ and give the following precipitates:

Alkali hydroxides form Sb_2O_3, white, not readily soluble in NH_4OH, soluble in fixed alkali hydroxide, forming salts such as $NaSbO_2$, containing the monovalent ion SbO_2'.

Hydrosulphuric acid (the **sulphur ion**) from a solution not too strongly acidulated precipitates Sb_2S_3, orange, soluble in strong HCl, scarcely at all in ammonium carbonate solution (distinctions from As_2S_3). The precipitate dissolves (in common with sulphides of As and Sn) in yellow ammonium sulphide, to form ammonium sulphantimonate, $(NH_4)_3SbS_4$, from which acids precipitate orange Sb_2S_5.

The solution of Sb_2S_5 in $(NH_4)_2S$ to form $(NH_4)_3SbS_4$ is exactly analogous to the solution of Sb_2O_5 in KOH to form K_3SbO_4, the Sb compound in each case playing the part of an acid. The higher oxide of an element has in general stronger acid properties than the lower, and the same is true of the sulphides; Sb_2S_3 does not dissolve in $(NH_4)_2S$ to form the corresponding sulphantimonite $(NH_4)_3SbS_3$. Only when sufficient sulphur is present, as in the polysulphides, for formation of the derivative of the higher sulphide, is Sb_2S_3 soluble in alkali. The lower sulphide of arsenic, As_2S_3, on the other hand, owing to the fact that arsenic is a more decidedly non-metallic (acid-forming) element than antimony, dissolves in normal alkali sulphide or in alkali hydroxide to form a soluble sulpharsenite.

57. In **Marsh's test**, conducted as directed for As in §**50,** the gas SbH_3 is obtained, but less readily than with As, black metallic Sb being first precipitated in the generator.

$$2SbCl_3 + 6Zn + 3H_2SO_4 = 2SbH_3 + 3ZnSO_4 + 3ZnCl_2$$

Passed into **$AgNO_3$** solution, black $SbAg_3$ precipitates:

$$SbH_3 + 3AgNO_3 = SbAg_3 + 3HNO_3$$

The filtered precipitate treated with hot HCl gives $SbCl_3$ and AgCl, the latter soluble in the strong acid. Dilute to pre-to the metal, globules if the material is in cons reduced metal reoxidizes readily to

Bismuth.

60. Bismuth forms a number of of their low melting-point, as Woc containing 15 parts of Bi, eight of of Cd. It is found in nature as the nitrate of bismuth, used in medic $BiONO_3$; pearl white and flake whit

61. Bismuth forms a very weakly salts on treatment with water hydr of white basic compounds. To prev the salts must be dissolved in dilute

62. **Hydroxide** of **fixed alkali** or of the **hydroxyl ion,** precipitates Bi(O excess (a separation from Cu if NH_4O

Alkali carbonate solution, contain **OH′**, precipitates a mixture of Bi(O subcarbonate of medicine.

Hydrosulphuric acid or a soluble **su** cipitates Bi_2S_3, black. A soluble **c** (ion **CrO_4''** or **Cr_2O_7''**) precipitates b

64. Heated on **charcoal** with Na_2CO_3 Bi compounds leave the metal as little lustrous globules, brittle under the knife or hammer (the brittleness a distinction from Pb). An incrustation of oxide, yellow when hot, almost white when cold, forms on the charcoal about the globules: $2Bi_2O_3 + 3C = 4Bi + 3CO_2$.

Copper.

65. Common forms: Metallic copper, useful as a good conductor of electricity; brass, an alloy of Cu and Zn; bronze, gun-metal, bell-metal, alloys of Cu and Sn; blue vitriol, $CuSO_4, 5H_2O$; true verdigris is a basic acetate; "copper-rust," sometimes called verdigris, is a basic carbonate; Paris green is an aceto-arsenite.

Mineralogy: Copper is found native; and as chalcocite or copper glance, Cu_2S; chalcopyrite or copper pyrites, Cu_2S, Fe_2S_3; bornite or purple copper, $3Cu_2S, Fe_2S_3$; cuprite or red oxide of copper, CuO; malachite and azurite, hydrated basic carbonates; and chrysocolla, a silicate.

66. Copper forms the monovalent cuprous and the divalent cupric ion, the former unstable; it is also a constituent of a number of complex ions. The cupric ion is blue, the non-dissociated salts are yellow; $CuCl_2$ solution dilute is blue, concentrated green, the result of the mixture of yellow and blue; the green solution becomes yellow on addition of strong HCl or on heating, for the reason that either of these causes increases the proportion of non-dissociated salt. Copper salts, when dissolved in water, are hydrolyzed sufficiently to redden litmus.

67. A cupric salt, with the ion $Cu^{\cdot\cdot}$, is precipitated by **alkali hydroxide (ion OH')**, as $Cu(OH)_2$, dark blue to black, insoluble in excess of fixed alkali hydroxides, easily soluble in excess NH_4OH with formation of the kathion $Cu(NH_3)_4^{\cdot\cdot}$ of intense blue color, a delicate test for Cu (delicacy 0.05 mg. Cu per cc.): $CuSO_4 + 4NH_4OH = Cu(NH_3)_4SO_4 + 4H_2O$. Precipitation of the hydroxide is prevented by organic substances containing the hydroxyl group (Fehling's solution).

Soluble **carbonates,** which contain both **CO_3''** and **OH' ions,** precipitate a mixture of carbonate and hydroxide, soluble in $(NH_4)_2CO_3$; **hydrosulphuric acid** or a soluble **sulphide** (the ion S'') precipitates CuS, black (delicacy 0.01 mg. per cc.), slightly soluble in ammonium sulphide; **ferrocyanides** precipitate brown $Cu_2Fe(CN)_6$ (delicacy 0.01 mg. per cc.); **KI** precipitates from cupric solutions CuI, with liberation of I; **KCN** precipitates from solutions of $Cu^{\cdot\cdot}$ cuprous cyanide, $CuCN$, with evolution of cyanogen gas: $2CuSO_4 + 4KCN = 2CuCN + (CN)_2 + 2K_2SO_4$. The precipitate dissolves in excess of the reagent, forming the colorless cuprocyanide anion: $CuCN + KCN = KCu(CN)_2$; the solution contains copper ions in such slight concentration that they are not precipitated even by H_2S. **Arsenites** (As_2O_3 neutralized with alkali) precipitate $CuHAsO_3$, Scheele's green; from copper acetate solution the precipitate is copper aceto-arsenite, Schweinfurth green, Paris green. The precipitates dissolve in NH_4OH and are decomposed by fixed alkali hydroxides.

68. A bright **iron** wire or nail or strip of **zinc** immersed in a solution of copper salt receives the red coating of metallic copper (delicacy 0.008 mg. per cc.): $CuSO_4 + Fe = Cu + FeSO_4$.

69. Heated on **charcoal** with Na_2CO_3 copper compounds are reduced to finely divided grains of the metal: $2CuSO_4 + 2Na_2CO_3 + C = 2Cu + 2Na_2SO_4 + 3CO_2$.

For the **bead** test, see § **248.**

Cadmium.

70. Cadmium occurs in nature in comparatively small quantity, associated with zinc; with Bi, Pb and Sn it is a constituent of Wood's metal; a cadmium amalgam is used by dentists for filling teeth; cadmium sulphide, CdS, "cadmium," or cadmia, is used as a yellow pigment.

71. Cadmium forms a divalent ion, weakly basic, its salts reddening litmus in water solution. Its halogen salts, the iodide in particular, are less completely dissociated than is usual with normal salts, and they therefore give precipitation reactions somewhat less readily than do the oxysalts.

72. **Alkali hydroxide** solution (the **ion OH′**) precipitates the Cd ion as $Cd(OH)_2$, white, dissolving in NH_4OH with formation of complex ions containing NH_3; **carbonate** solution (the **ion CO_3''**) precipitates $CdCO_3$, white; solution of **H_2S** or of **a sulphide (ion S″)** precipitates CdS, yellow, somewhat less readily soluble in acid than ZnS; **KCN** precipitates $Cd(CN)_2$, white, dissolving in excess of the reagent to $K_2Cd(CN)_4$ (ions $2K^{\cdot}$ and $Cd(CN)_4''$), in which, however, the concentration of Cd ions is great enough for precipitation with H_2S (method of separation from Cu).

73. Heated on **charcoal** with Na_2CO_3 Cd compounds give the metal, which vaporizes and reoxidizes to a brown incrustation of CdO.

Gold.

74. Gold coin is an alloy containing about 10 per cent Cu for hardening; 18-carat gold is one-third Cu, the number of carats giving the parts of gold in 24 parts of alloy; $AuCl_3$ is used for toning photographs, metallic gold depositing; the "gold salt" used in photography is $NaAuCl_4, 2H_2O$.

75. Gold acts feebly both as acid and as base. The ions $Au^{\cdot}$ and $Au^{\cdot\cdot\cdot}$ are unstable and little known. Complex anions containing the mono- or trivalent metal form its most stable compounds. Pure gold does not dissolve in HNO_3; an alloy with Cu or Ag containing not over 20 per cent Au is disintegrated by HNO_3, the Au separating as a brown powder. Nitro-hydrochloric acid or free chlorine forms a solution from which $HAuCl_4$ (hydro-aurichloric acid) may be crystallized, changing to $AuCl_3$ and HCl on heating. Further heating liberates Cl, leaving AuCl. $AuCl_3$ is freely soluble; AuCl breaks up on contact with water: $3AuCl = AuCl_3 + 2Au$. KCN in the presence of air dissolves the metal (the cyanide process of extraction from the ore): $2Au + 8KCN + 2O_2 + 4H_2O = 2KAu(CN)_4 + 6KOH + H_2O_2$.* From this solution the metal is obtained by electrolysis or by precipitation with zinc.

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* Ostwald, Grundlinien der anorganischen Chemie, p. 754.

76. **Fixed alkali hydroxide** (the **OH′ ion**) precipitates from auric solutions $Au(OH)_3$, yellow-brown, forming with excess soluble aurates, as $KAuO_2$; **NH_4OH** precipitates reddish-yellow "fulminating gold." The **sulphur ion** of **H_2S** precipitates brown to black sulphides, Au_2S to Au_2S_2, with sulphur, slowly soluble in alkali sulphide to sulpho-salts, reprecipitated by acid.

77. **Reducing agents,** as **$FeSO_4$** and **$H_2C_2O_4$**, precipitate the metal, brown to violet; with $SnCl_2$ the precipitate is the "purple of Cassius" and carries oxides of tin.

78. Gold compounds give the metal on **heating.**

Platinum.

79. Platinum black is the finely divided metal obtained by reduction from solution; platinum sponge results on heating Pt compounds, as $(NH_4)_2PtCl_6$. Platinum occurs in nature as metallic grains or nuggets.

80. As in the case of gold, the complex ions are the stable ones, those containing the tetravalent Pt being more common than those containing the divalent. Pt is insoluble in HNO_3 or concentrated H_2SO_4; nitro-hydrochloric dissolves it, forming H_2PtCl_6; this compound on heating gives off HCl, forming $PtCl_4$, readily soluble in water. Platinic compounds give by reduction the platinous, as $PtCl_2$, soluble in HCl to H_2PtCl_4.

81. **KOH** gives with H_2PtCl_4 $Pt(OH)_2$, redissolving to K_2PtO_2; with H_2PtCl_6 the yellow crystalline K_2PtCl_6, one of the very few insoluble K salts known, forms; the corresponding **ammonium** compound is also insoluble, that of **sodium** soluble; H_2PtCl_6 is better precipitated by **KCl** or **NH_4Cl**. **H_2S** gives PtS or PtS_2, black, slowly soluble in alkali sulphides.

82. **Reduction** is not effected by **$H_2C_2O_4$** (distinction from Au), but results slowly with **$FeSO_4$** and rapidly with **Zn**, or with **alcohol** in alkaline solution (K_2PtO_2), the metal appearing in each case as a black powder.

83. All Pt compounds on **heating** give the metal as porous Pt-sponge.

84. Analysis of the Silver Group (Pb, Ag, $Hg^{\cdot}$).

To the solution add HCl, a drop at a time, as long as precipitation occurs; shake and filter. Reserve the filtrate for Group II. (§87).

Precipitate: **$PbCl_2$, AgCl, HgCl**.

Wash the precipitate, on the paper, with a little cold water, rejecting the wash-water; then treat with hot water.

Filtrate, $PbCl_2$.	Residue, AgCl, HgCl.	
Test separate portions with:	**Digest on the paper with a little warm dilute NH_4OH.**	
H_2SO_4, precipitating $PbSO_4$, white, soluble in NaOH;	**Filtrate,**	**Residue,**
H_2S, precipitating PbS, black;	**$(NH_3)_2AgCl$. Acidify with HNO_3, precipitating AgCl, white, darkening in light.**	**$NH_2HgCl + Hg$, black. Basic Pb salt, white.**
$K_2Cr_2O_7$, precipitating $PbCrO_4$, yellow;		
KI, precipitating PbI_2, yellow.		

85. To filter, fold the paper and place in the funnel (it should not project over the rim), moisten it, and fit it down to the sides of the funnel so closely as to make it air-tight. Filtration will be more rapid if the stem of the funnel can be kept filled with liquid. A precipitate may be washed first by decantation, boiling up with water and then allowing to settle, and pouring the clear liquid upon the paper, disturbing the precipitate as little as possible. More water is added and the boiling repeated. On the filter, after the liquid from which the precipitate is being separated has drained off as completely as possible, water is run in a fine stream from the wash-bottle or, if hot, poured from the test-tube, around the rim of the paper until the precipitate is covered. When this has drained away repeat the operation. Test small portions of the wash-water for the substance which is to be removed and continue washing until the water running off no longer gives this test. Hot water is more efficacious for washing than cold. For theory of washing, see Ostwald, Scientific Foundations of Analytical Chemistry, 2nd Ed., p. 17.

To dissolve a precipitate on the filter, add a small portion of the solvent, which may in most cases be warmed, and receive in a clean test-tube or small beaker. An excess of the solvent is nearly always a disadvantage to subsequent work. Changing the receiver, the same portion of the solvent may be passed through the filter again and again till nearly saturated. Finally the solution remaining in the paper may be saved by washing it out with one or two small portions of water. To dissolve the precipitate in a test-tube (better where the solvent acts slowly): Pierce the paper with a pointed glass rod kept for that purpose, and rinse the precipitate through into a clean test-tube; here also the same portion of solvent should be put repeatedly through the filter, finally rinsing with a few drops of water. The liquid is now warmed in the test-tube and filtered to remove paper fiber and undissolved residue.

86. Notes.—*a.*—The solution to be tested must not be strongly acid. Remove excess by evaporation. The chlorides are less soluble in dilute HCl than in water (solubility-product), but more soluble in concentrated HCl, owing to the formation of complexes, as $HAgCl_2$. $PbCl_2$ is about one-ninth as soluble in normal HCl as in water; with acid of greater concentration its solubility increases.

b.—Precipitation with HCl may occur even though no Silver-Group metal is present. Oxychlorides of Bi, Sb or Sn sometimes form, readily dissolving with more acid. In concentrated solution moderately soluble chlorides, as $BaCl_2$ or $HgCl_2$, may precipitate. These are soluble on diluting. Solution of metallic hydroxide, sulphide, etc., in alkali is decomposed by acid, with precipitation. If HCl in slight excess fails to dissolve such precipitates they must, after filtering, be treated with other solvents and analyzed separately.

c.—Mercuric salts, with the ion $Hg^{\cdot\cdot}$, hinder precipitation of Silver-Group metals, the chlorine ion of the added HCl being taken up to form non-dissociated $HgCl_2$.

d.—If $PbCl_2$ is not completely dissolved by hot water the addition of NH_4OH will form insoluble white basic lead chloride.

e.—If the ammoniacal solution comes through turbid filter it through a fresh paper. It is not advisable to pass it repeatedly through the paper on which Hg has been precipitated, for if Ag is present the following change may take place leaving Ag on the filter: $Hg + (NH_3)_2AgCl + 2H_2O = Ag + HgCl + 2NH_4OH$. Avoid excess of NH_4OH, as it dissolves NH_2HgCl, which may be reprecipitated by HNO_3, simulating Ag.

87. Analysis of the Tin and Copper Group.

Neutralize the filtrate from Group I. with **NH_4OH**, then add **HCl** until the acid is about N/2 (it must not be stronger). Heat, pass **H_2S** gas, and filter. Reserve the filtrate for the Iron Group.

Precipitate: **As_2S_3** or **As_2S_5** (yellow), **Sb_2S_3** or **Sb_2S_5** (orange), **SnS** (brown), **SnS_2** (yellow), **PbS** (black), **HgS** (finally black), **Bi_2S_3** (black), **CuS** (black), **CdS** (yellow), **S** (white).

Wash the precipitate thoroughly with **H_2S** solution and digest with **yellow ammonium sulphide.** Filter. Reserve the residue for the Copper Subgroup.

Solution: **$(NH_4)_3AsS_4$**, **$(NH_4)_3SbS_4$**, **$(NH_4)_2SnS_3$**.

Acidulate with dilute **HCl**, filter and wash.

Precipitate: **Tin Subgroup, As_2S_5, Sb_2S_5, SnS_2, S**.

Digest the washed precipitate in a test-tube with hot **HCl** (and if necessary a minute fragment **$KClO_3$**) until the precipitate is dissolved or decolored. Filter out any sulphur, receive the filtrate (**H_3AsO_4**, **$SbCl_5$**, **$SnCl_4$**) in an evaporating dish, and heat to expel chlorine. Transfer to flask containing **Zn** and dilute **H_2SO_4** (Marsh apparatus) and receive all the gas (AsH_3, SbH_3) in **$AgNO_3$** solution. Filter the silver solution and wash the precipitate.

Residue in the generator: **Sn**, (**Sb**, **Zn**).	Precipitate from **$AgNO_3$**: **$SbAg_3$**, **Ag**.	Filtrate: **H_3AsO_3** (**$AgNO_3$**, **HNO_3**).
Sn separates as grayish, leathery flakes; filter, dissolve these in **HCl** and test with **$HgCl_2$**, precipitating **Hg**, gray, or **HgCl**, white. Test original solution by §44.	Treat on the filter with warm **HCl**. Dilute the filtrate (to precipitate **AgCl**), filter again if necessary, and to one portion of the solution add **H_2S**; an orange precipitate is **Sb_2S_3**. If the precipitate is black (**Ag_2S**) add to a second portion of the solution a drop of **KI**, precipitating **AgI**; filter and add **H_2S**, ppting **Sb_2S_3** if **Sb** is present.	Add **$CaCl_2$** to completely precipitate silver ($Ag^\cdot$) as the chloride, filter, and pass **H_2S** into filtrate; a yellow precipitate is **As_2S_3**.

88. Notes.—*a.*—Before testing for Second-Group metals make sure of the complete removal of the Silver Group by adding to the filtered solution a drop of HCl. Such a test should always be made after a precipitation.

b.—A white precipitate on adding NH_4OH preparatory to precipitation of this group may be neglected and the H_2S passed into the turbid acid solution; the hydroxides so formed are converted into the sulphide owing to the slighter solubility of the latter.

c.—It is of the utmost importance that the solution contain but little mineral acid when the Tin and Copper Group is precipitated. A glance at the equilibrium equation shows the effect on the S ions of addition of 2N HCl, with $[H^\cdot] =$ perhaps 1.7, to H_2S, with $[H^\cdot] =$ say 0.001. $[H^\cdot]^2[S''] = k[H_2S]$. $[H^\cdot]$ will be enormously increased by addition of the HCl, and $[S'']$ must decrease correspondingly, thus making precipitation of sulphides difficult, for $[S'']$ is one of the factors of the solubility-product of sulphides. If not removed here these metals will appear in following groups and cause confusion. $CdCl_2$ in N/2 HCl is completely precipitated by H_2S; to prevent precipitation of ZnS the acid should be as strong as N/8.

d.—A strongly acid solution saturated with H_2S may give a precipitate of sulphides simply on diluting with water. This is due to the fact that H_2S, like all feebly dissociated substances, increases its percentage of dissociation very decidedly on dilution. Addition of water may in this way actually increase the absolute concentration of the S ions, while it decreases the concentration of the H ions of the strong acid, this also aiding the dissociation of the H_2S.

e.—Strong oxidizing agents if present are reduced by H_2S with precipitation of sulphur. Ferric compounds, yellow, and MnO_4', the purple ion of permanganates, thus become colorless, while Cr_2O_7'', the red ion of dichromates, is changed to $Cr^{\cdot\cdot\cdot}$, green.

f.—A white precipitate with excess of H_2S is either S or ZnS; if the latter it will dissolve readily in HCl; in either case proceed to the next group after adding more acid. If zinc is precipitated with sulphides of this group it will appear as a white sulphide in the final test for Cd, from which it may be separated by the greater solubility of ZnS in HCl.

g.—H_3AsO_4 requires heat and prolonged treatment with H_2S for complete precipitation.

h.—Mercuric salts ($Hg^{\cdot\cdot}$) give with H_2S at first a white precipitate, becoming yellow, brown, and finally, with excess of H_2S, black. Pb gives a red precipitate in the presence of too much acid.

i.—If metals of the Tin Subgroup are absent, a perfectly white precipitate of sulphur is obtained with HCl from the ammonium polysulphide solution (it may appear yellow with insufficient HCl owing to the color of the ammonium polysulphide). In presence of Cu the precipitate is liver-colored, due to a slight solubility of CuS in ammonium sulphide.

Fixed alkali polysulphide does not dissolve CuS and may be used instead of the ammonium compound if Hg is not present; it dissolves HgS.

j.—A trace of Sb goes into solution on passing the gas SbH_3 into $AgNO_3$ and gives with H_2S a slight orange precipitate, which must not be mistaken for As_2S_3.

k.—Metallic tin is not dissolved by acid so long as a more positive metal, as zinc, is present. (See voltaic series, §27.) If the zinc is allowed to dissolve completely the tin will then go into solution.

l.—Au and Pt belong to this group and are precipitated in the metallic form in the Marsh generator. They are best identified by boiling the original solution with $FeSO_4$, precipitating both, then dissolving in nitro-hydrochloric acid and evaporating to dryness on the water-bath with NH_4Cl. Alcohol dissolves NH_4AuCl_4 from the residue, leaving $(NH_4)_2PtCl_6$, which gives metallic Pt on heating. After driving off the alcohol Au is precipitated as purple of Cassius with $SnCl_2$ and $SnCl_4$.

89. Copper Subgroup. (HgS, PbS, Bi_2S_3, CuS, CdS, S).

The well-washed precipitate is boiled with dilute (2N) HNO_3.

<table>
<tr>
<td rowspan="5">Residue: HgS (bl'k), S. Dissolve in nitrohydrochloric acid and boil to expel free Cl. Solution, $HgCl_2$. Add $SnCl_2$, precipitating HgCl, white, or Hg, gray.</td>
<td colspan="6">Filtrate: Nitrates of Pb, Cu, Cd, Bi. Evaporate almost dry in the porcelain dish to free from HNO_3, take up with hot water, and filter.</td>
</tr>
<tr>
<td rowspan="4">Residue: Basic Bi salts. Wash and add to the precipitate on the paper hot Na_2SnO_2 solution, producing black metallic Bi, § 63.</td>
<td colspan="5">Filtrate: Nitrates of Pb, Cu, Cd, [Bi]. Add dilute H_2SO_4, shake, and allow to stand.</td>
</tr>
<tr>
<td rowspan="3">Precipitate: $PbSO_4$, white, sol. in NaOH.</td>
<td colspan="4">Filtrate: Nitrates of Cu, Cd, [Bi]. Add NH_4OH.</td>
</tr>
<tr>
<td rowspan="2">Precipitate: $Bi(OH)_3$, white. Wash and test with stannite, as above.</td>
<td rowspan="2">A blue color in the filtrate is evidence of Cu. Decolor with KCN and pass in H_2S; a yellow to green precipitate is CdS.</td>
<td colspan="2">If the filtrate is colorless divide into two portions.</td>
</tr>
<tr>
<td>In one portion test for traces of Cu by concentrating by evaporation, acidifying with acetic acid, and adding $K_4Fe(CN)_6$. A brown precipitate is $Cu_2Fe(CN)_6$.</td>
<td>Into the other portion pass H_2S. A yellow to green precipitate is CdS.</td>
</tr>
</table>

90. Notes.—*a.*—$PbCl_2$ is so much more soluble than PbS that its saturated solution gives a decided precipitate with H_2S. If Pb is found in the Silver Group it must therefore be found in this group also; or it may be found in this group only.

b.—The sulphur liberated on dissolving the sulphides in HNO_3 encloses a portion of them, giving even though mercury is not present a black spongy mass which resists the action of acid. The only safe procedure is always to dissolve any black residue in nitro-hydrochloric and test for mercury (the ion $Hg^{\cdot\cdot}$).

c.—If the HNO_3 is taken too strong some HgS will dissolve; on adding NH_4OH the $Hg^{\cdot\cdot}$ will give a white precipitate which blackens on addition of stannite, owing to formation of Hg. $Pb^{\cdot\cdot}$ also, if not completely removed, will simulate $Bi^{\cdot\cdot\cdot}$, precipitating with NH_4OH as a white basic salt, reduced to dark-colored metallic Pb by stannite. A drop of KNO_2 solution (free from Cl') aids materially in dissolving the sulphides by dilute HNO_3.

d.—$PbSO_4$ is decidedly soluble in HNO_3, 1 cc. of the strength used here dissolving about 3 mg. $PbSO_4$; it dissolves also in NH_4NO_3 solution and it is therefore necessary to remove all ammonium sulphide by thorough washing.

e.—If the original solution contains Ba traces are likely to adhere to the sulphides and give $BaSO_4$ on testing for Pb. The precipitate should be treated with NaOH, which dissolves $PbSO_4$ but not $BaSO_4$.

f.—The precipitation of $Cu_2Fe(CN)_6$ is more delicate than the blue coloration with NH_4OH. $Cd_2Fe(CN)_6$ is white.

91. Exercises with Ions of the Silver and Tin and Copper Groups.*

Carry out for each metal the reactions discussed in the text, writing equations for all changes.

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*These exercises are simply suggestive and should be modified and extended to meet the needs of individual classes.

Identify each metal (kathion) in a solution of its salt, treating it as an unknown substance as in the tables §§**87** and **89**. Write equations as far as possible.

Separate and identify the metals (kathions) in mixtures of solutions of the following salts, following the tables at §§**87** and **89**:

$Pb(NO_3)_2$, $AgNO_3$.
$Pb(NO_3)_2$, $HgNO_3$.
$AgNO_3$, $HgNO_3$.
$Pb(NO_3)_2$, $AgNO_3$, $HgNO_3$.
$Pb(NO_3)_2$, $Bi(NO_3)_3$, $Cu(NO_3)_2$.
$PbCl_2$, $HgCl_2$.
H_3AsO_3, $SbCl_3$ (with HCl).
$CdCl_2$, H_3AsO_3.
$BiCl_3$, $SbCl_3$.
H_3AsO_3, $SbCl_3$, $SnCl_2$.

Test so-called chemically pure $CuSO_4$ solution for As; $SbCl_3$ solution for As; $HgNO_3$ solution for $Hg^{\cdot\cdot}$; $Pb(NO_3)_2$ solution for $Ag^{\cdot}$; $Hg(NO_3)_2$ solution for $Bi^{\cdot\cdot\cdot}$.

Separate the bases (kathions) in the following mixtures, using methods other than those given in the tables:

$Pb^{\cdot\cdot}$ from $Ag^{\cdot}$ (with dilute H_2SO_4).

$Ag^{\cdot}$ from $Bi^{\cdot\cdot\cdot}$ (with NH_4OH); identify the $Ag^{\cdot}$.

$Cu^{\cdot\cdot}$ from $Cd^{\cdot\cdot}$ (treat the sulphides with dilute H_2SO_4).

As from $Sb^{\cdot\cdot\cdot}$ (digest the sulphides with ammonium carbonate solution; test the solution and the residue for both $Sb^{\cdot\cdot\cdot}$ and As).

Ascertain the delicacy of the precipitation of $Ag^{\cdot}$ with Cl', that is, the strength of the solution of $AgNO_3$ which will just give a perceptible opalescence with a drop of dilute HCl. Take 1 cc. N/4 $AgNO_3$ solution, add 9 cc. water, reducing concentration to N/40; test a portion of this with HCl; if a precipitate is obtained take 1 cc. of the N/40 solution, dilute to 10 cc., and repeat the test in a portion of this N/400 solution; continue in this way until a solution is obtained which gives no reaction with HCl. How many milligrams of Ag per cc. of solution may be detected with HCl?

The presence of how little $Pb^{\cdot\cdot}$ may be shown by precipitation with H_2S?

Dilute the $AgNO_3$ solution with N/2 $Cd(NO_3)_2$ solution instead of with water. How does this affect the delicacy? Why? Use also $Hg(NO_3)_2$; $NaNO_3$.

Find by experiment how HNO_3 affects the delicacy of the precipitation of $Pb^{\cdot\cdot}$ with dilute H_2SO_4. The same for NH_4NO_3.

How does strong HCl affect the delicacy of the precipitation of Cu by H_2S? of As?

Ascertain how little $Ag^{\cdot}$ may be found in the presence of N/2 $Pb^{\cdot\cdot}$, following the method of separation and identification given in the table §87. How little $Ag^{\cdot}$ in the presence of N/2 $HgNO_3$? How little $Pb^{\cdot\cdot}$ in the presence of N/2 $Bi^{\cdot\cdot\cdot}$?

92. Metals of the Iron and Zinc Groups in the Periodic System.

Li 7	Be 9	B 11	C 12	N 14	O 16	F 19	
Na 23	Mg 24.4	Al 27	Si 28.4	P 31	S 32	Cl 35.5	
K 39	Ca 40	Sc 44	Ti 48	V 51	Cr 52	Mn 55	Fe 56, Ni 58.7, Co 59
Cu 63.6	Zn 65.4	Ga 70	Ge 72	As 75	Se 79	Br 80	
Rb 85.4	Sr 87.6	Y 89	Zr 90.6	Cb 94	Mo 96		Ru 102, Rh 103, Pd 106
Ag 108	Cd 112	In 114	Sn 118.5	Sb 120	Te 127	I 127	
Cs 133	Ba 137.4	La 138 etc.					
		Yb 173		Ta 183	W 184		Os 191, Ir 193, Pt 195
Au 197	Hg 200	Tl 204	Pb 207	Bi 208			
			Th 232		U 240		

Iron and Zinc Groups.

93. Groups III. and IV.—Metals precipitated by $(NH_4)_2S$, not by H_2S in acid solution: Fe, Cr, Al, [Si], Co, Ni, Mn and Zn, and, of rarer occurrence: Sc, Y, La, Ce, Pr, Nd, Sm, Yb, Ga, In, Tl, Ti, Zr, Th, Cb, Ta, U.

The metals here enumerated are more electropositive (base-forming) in character than those of the preceding groups, suffering oxidation more readily and undergoing reduction from their compounds with greater difficulty. Nearer the positive end of the voltaic series than hydrogen, they replace the latter, dissolving in acids, as HCl or H_2SO_4, with evolution of hydrogen. They are still so feebly basic that their salts in water solution have acid reaction resulting from hydrolysis. They are not precipitated by H_2S from acid solution (separation from the preceding groups), but are precipitated by the more completely dissociated neutral sulphides. The trivalent metals Fe, Al and Cr of the Iron Group are precipitated completely as hydroxides by NH_4OH in the presence of NH_4Cl, a useful separation from the metals of the Zinc Group (Co, Ni, Mn and Zn).

Iron.

94. Wrought iron, as in fine iron wire, is the purest form in common use; steel contains a little carbon in combination as carbide, with Mn, Si, etc., in very small quantity; cast iron contains more carbon, both combined and free, with various impurities. Green vitriol is $FeSO_4,7H_2O$, copperas; FeS is the material used for generating H_2S in the laboratory. Occurrence in nature: Red hematite, specular iron ore, rouge, red ocher, are ferric oxide, Fe_2O_3; magnetic iron ore or lodestone is ferroferric oxide, Fe_3O_4; limonite or yellow ocher is hydrated oxide; spathic ore, siderite, is ferrous carbonate; iron pyrites is the disulphide, FeS_2.

95. Iron dissolves in HCl or in dilute H_2SO_4 to the ferrous ion, $Fe^{\cdot\cdot}$; in HNO_3 to the ferric ion, $Fe^{\cdot\cdot\cdot}$. Both are weakly basic and their salts have acid reaction in water solution. The metal forms a number of complex ions: FeO_4'' of ferrates, as Na_2FeO_4, made by oxidizing action of halogens, is stable only in the presence of fixed alkali hydroxide; ferrocyanides, as $K_4Fe(CN)_6$, and ferricyanides, as $K_3Fe(CN)_6$, contain, respectively, the ferrocyanogen and ferricyanogen ions, $Fe(CN)_6''''$ and $Fe(CN)_6'''$.*

96. Ferrous salts, containing the **ion** $\mathbf{Fe^{\cdot\cdot}}$ when in solution, are precipitated by **alkali hydroxide** (the **ion** $\mathbf{OH'}$) as $Fe(OH)_2$, white when pure, usually greenish to black from partial oxidation, changing slowly in air to brown $Fe(OH)_3$. With $\mathbf{NH_4OH}$ the precipitation is but partial, the ammonium salt formed decreasing the hydroxyl ion concentration so that a comparatively large concentration of the ferrous ion is required to give the solubility-product.

Carbonates, containing the **ion** $\mathbf{CO_3''}$, precipitate $FeCO_3$, soon darkening from oxidation.

Soluble **sulphides**, containing the **sulphur ion** in considerable concentration, not $\mathbf{H_2S}$, precipitate FeS, black.

Phosphates precipitate $FeHPO_4$ with $Fe_3(PO_4)_2$.

Ferricyanides, as $\mathbf{K_3Fe(CN)_6}$, precipitate ferrous ferricyanide, $Fe_3[Fe(CN)_6]_2$, intensely blue, important as a distinction from ferric salts, which give no precipitate, although darkening the solution or turning it green. $K_4Fe(CN)_6$ precipitates $K_2FeFe(CN)_6$, white, becoming blue from oxidation. Both these precipitates are insoluble in dilute acids but decomposed by alkalis. Sulphocyanates give no color with ferrous salts which are quite free from ferric.

97. Ferric salts are to some extent hydrolyzed by water and their solutions contain $Fe(OH)_3$, dissolved in the colloid form, and free acid: $FeCl_3 + 3H_2O = Fe(OH)_3 + 3HCl$.

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* The ferrocyanides and ferricyanides contain neither the ferrous nor the ferric ion in appreciable quantity, as is evident from the fact that they do not yield the ordinary reactions of ferrous or ferric salts. The iron is present in these compounds as a complex anion, $Fe(CN)_6$, in the one case trivalent and in the other case tetravalent. Hence the possibility, as Ostwald points out, of using as a reagent for iron a compound containing iron.

The iron is completely precipitated by a soluble **hydroxide** as red-brown $Fe(OH)_3$; the precipitation is prevented by certain organic substances such as sugar, with which the ferric ion combines to form a complex. The precipitate with soluble **carbonates** contains but little ferric carbonate, practically complete hydrolysis taking place into $Fe(OH)_3$ and CO_2.

H_2S causes reduction to ferrous salt (the ion $Fe^{\cdot\cdot}$) with precipitation of sulphur only. Soluble **sulphides** precipitate FeS, black, mixed with free sulphur.

Phosphates precipitate $FePO_4$, white, scarcely soluble in acetic acid, a distinction from phosphates of the alkaline earth metals, which are soluble in acetic acid.

Sulphocyanates, as **KCNS**, form a deep red solution of $Fe(CNS)_3$. Delicacy ca. 0.002 mg. Fe per cc. The color is due to the non-dissociated substance and is intensified by agents which decrease the dissociation, as KCNS in excess. Acid intensifies the color by preventing hydrolysis. $HgCl_2$, on the other hand, destroys the color by forming the non-dissociated $Hg(CNS)_2$. Such salts as Na_2SO_4 weaken the color by taking up some of the iron as $Fe_2(SO_4)_3$.

Ferrocyanides precipitate deep blue ferric ferrocyanide, $Fe_4[Fe(CN)_6]_3$, prussian blue, insoluble in dilute acid, decomposed by alkalis.

Soluble **acetates**, as $NaC_2H_3O_2$, with ferric salts in neutral or slightly acid solution form ferric acetate, giving a dull-red color to the liquid without precipitation. Raising the temperature, which always increases hydrolysis, causes the separation of a basic ferric acetate. **Tannic acid** and **tincture of galls** precipitate blue-black ferric tannate, formerly extensively used for black ink. **Salicylic acid** gives a deep violet color.

98. Iron salts are generally decomposed by **heat**; $FeCl_3$ vaporizes undecomposed at a little above 100° C. Heated in the air on **charcoal** both ferrous and ferric compounds are converted to Fe_3O_4, attracted by the magnet.

99. Distinctions between Fe··· and Fe··.

	Fe···.	Fe··.
Ferricyanides ($Fe(CN)_6'''$)	No precipitate; green color.	Deep blue precipitate.
Ferrocyanides ($Fe(CN)_6''''$)	Deep blue precipitate.	White precipitate, becoming blue.
Sulphocyanates (CNS')	Red solution.	No change.*
Carbonates (CO_3'' and OH')	$Fe(OH)_3$ precipitated.	$FeCO_3$ precipitated.
Cyanides (CN')	$Fe(OH)_3$ precipitated.	Ferrocyanide formed with CN' in excess.

Oxidizing agents change Fe·· to Fe···:

HNO_3		Gives off brown gas.
Cl water		Is deodorized.
Br water		Is deodorized.
$KMnO_4$		Is decolored.

Reducing agents change Fe··· to Fe··:

H_2S	Is deodorized with precipitation of S.	
H_2SO_3	Is deodorized.	

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*Ferrous salts on standing give some reaction for Fe··· owing to slight oxidation.

The student is recommended to carry out these processes of oxidation and reduction, testing for Fe··· and Fe·· before and after the operation.

Aluminum.

100. Aluminum, made electrolytically from bauxite, an impure oxide-hydroxide, is in use as the metal and alloyed with 10 per cent copper in aluminum bronze. Potash alum, crystalline, is $KAl(SO_4)_2$, $12H_2O$; ammonia alum, the common "alum," used in cheap baking-powder, $NH_4Al(SO_4)_2$, $12H_2O$; concentrated alum is $Al_2(SO_4)_3$; this and the alums are used as mordants in dyeing. The varieties of clay are hydrated aluminum silicates, formed by action of weather on the feldspars, which are double silicates of aluminum with K, Na and Ca. Corundum, sapphire, oriental ruby and emerald are Al_2O_3. Emery is impure Al_2O_3; turquoise is a phosphate; cryolite is Na_3AlF_6.

101. Aluminum forms a trivalent kathion very weakly basic, and also weak anions, AlO_2' and AlO_3'''. It forms further complex ions with acids, sugar, glycerine, and other organic compounds containing the hydroxyl group, and its precipitation as hydroxide is prevented by the presence of these substances.

102. Alkali hydroxide (the **ion OH'**) precipitates aluminum salts (the ion $Al^{\cdot\cdot\cdot}$) from solution as gelatinous $Al(OH)_3$, soluble in fixed alkalis to form $NaAlO_2$ or Na_3AlO_3 with the feeble anions AlO_2' or AlO_3'''. Hydrolysis of the salts of these anions can be prevented only by the presence of the ion OH' in excess. Such a solution of Na_3AlO_3 in the presence of NaOH is therefore destroyed by **ammonium salt** (the ammonium ion), which takes up OH ion to form non-dissociated NH_4OH, and causes the precipitation by hydrolysis of $Al(OH)_3$, which here acts as a weak acid. In the same way the slight solubility of $Al(OH)_3$ in NH_4OH is decreased by the presence of $NH_4^{\cdot}$.

When a soluble **sulphide** or **carbonate** is added to a solution of aluminum salt the precipitate, owing to hydrolysis, is almost pure $Al(OH)_3$, H_2S or CO_2 being liberated. **$Na_2S_2O_3$** gives the same precipitate, the $H_2S_2O_3$ formed breaking up into SO_2, S and H_2O; this is a separation from iron.

Soluble **phosphate** (the **ion PO_4'''**) precipitates $AlPO_4$, soluble in fixed alkali hydroxide, not in dilute acetic acid.

103. Before the blowpipe on **charcoal** with Na_2CO_3 aluminum compounds leave the oxide, not reducible to the metal in this way. The oxide moistened with **$Co(NO_3)_2$** solution and strongly heated takes on a blue color.

Chromium.

104. Chromic oxide, Cr_2O_3 (chrome green), and lead chromate, $PbCrO_4$ (chrome yellow), are used in painting; red chromate of potash is potassium dichromate, $K_2Cr_2O_7$; yellow chromate of potash is potassium chromate, K_2CrO_4; chrome alum is $KCr(SO_4)_2,12H_2O$; $K_2Cr_2O_7$ is used in tanning; CrO_3

is used as an oxidizer. Chromium is found in chrome iron ore, chromite, Cr_2O_3,FeO.

105. Chromium forms a violet basic ion, $Cr^{\cdot\cdot\cdot}$, and also certain kathions of green color which contain acid radical as well as metal. Corresponding to these are the violet and green modifications of the solid salts.* It forms further the divalent acid ions Cr_2O_7'', red, and CrO_4'', yellow, derived from the oxide CrO_3, the former stable only in the presence of $H^{\cdot}$, the latter only in the presence of OH'. Organic compounds, as in the case of Al, form complex ions from which Cr is not precipitated by the usual reagents.

106. Solutions of **chromic** salts, containing the **ion $Cr^{\cdot\cdot\cdot}$**, are precipitated by soluble **hydroxides** (the **ion OH'**) as chromic hydroxide, $Cr(OH)_3$, green, forming with excess of fixed alkali hydroxide an unstable solution from which $Cr(OH)_3$ deposits slowly in the cold, rapidly on boiling. The precipitate is slightly soluble in NH_4OH, reddish chrome-ammonium ions forming. As in the case of Al the precipitate with **carbonates** and with **sulphides** is hydrolyzed and consists almost wholly of $Cr(OH)_3$. Soluble **phosphate** (the **ion PO_4'''**) precipitates $CrPO_4$, insoluble in acetic acid; **oxalates** cause no precipitation.

107. Chromic compounds are oxidized to yellow **chromate** by fusion with **KNO_3** or **$KClO_3$**, or by boiling with HNO_3 and **$KClO_3$**. The change is characteristic and is used for detection of Cr, the chromate being identified by precipitation of $PbCrO_4$ in presence of acetic acid.

The chromate ion, CrO_4'', takes up H ions to form the dichromate ion: $2CrO_4'' + 2H^{\cdot} = Cr_2O_7'' + H_2O$. Addition of acid to a normal chromate therefore changes it to the dichromate. CrO_3 dissolved in water forms dichromic acid,

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* $Cr_2(SO_4)_3$ heated with H_2SO_4 forms chromi-sulphuric acids which give no precipitate with Ba salts; from freshly-prepared solution of green chromic chloride but part of the chlorine is precipitated by $AgNO_3$. On standing, the violet ion forms slowly from the green, and so the ordinary green solutions give the reactions for $Cr^{\cdot\cdot\cdot}$. The violet $CrCl_3$, prepared by sublimation, is dissolved with difficulty by water.

$H_2Cr_2O_7$, and but little chromic acid, H_2CrO_4. With the hydroxyl ion, on the other hand, the dichromate ion reacts to form the normal chromate ion: $Cr_2O_7'' + 2OH' = 2CrO_4'' + H_2O$. Alkali therefore forms the yellow normal chromate from the red dichromate.

A soluble **chromate** (the **ion** $\mathbf{CrO_4''}$) gives with **lead** salts (ion **Pb**$^{\cdot\cdot}$) a yellow precipitate of $PbCrO_4$; with **barium** salts (ion **Ba**$^{\cdot\cdot}$), $BaCrO_4$, light yellow; with silver salts (ion **Ag**$^{\cdot}$), Ag_2CrO_4, dark reddish; with **mercurous** salts (**ion Hg**$^{\cdot}$), Hg_2CrO_4, brick-red. Solutions of dichromate contain sufficient of the CrO_4 ion to give the same precipitations.

108. Chromates are **deoxidized** to the green chromic salts (ion $Cr^{\cdot\cdot\cdot}$) by $\mathbf{H_2S}$ in acidulated solutions (as in precipitation of the Tin and Copper Group), with separation of sulphur; **ammonium sulphide** reduces the chromate and precipitates $Cr(OH)_3$: $K_2Cr_2O_7 + 3H_2S + 8HCl = 2CrCl_3 + 2KCl + 3S + 7H_2O$.

In analysis of a solution containing chromate, it is best reduced by boiling with alcohol in HCl solution before the Tin and Copper Group precipitation is made. HCl alone, when concentrated, will cause this reduction: $K_2CrO_4 + 8HCl = CrCl_3 + 2KCl + 3Cl + 4H_2O$.

Ferrous salt (**ion Fe**$^{\cdot\cdot}$) reduces chromate, a reaction employed in the volumetric estimation of iron: $K_2Cr_2O_7 + 6FeCl_2 + 14HCl = 2CrCl_3 + 6FeCl_3 + 2KCl + 7H_2O$.

109. Chromates and most other Cr compounds, heated on **charcoal**, leave a green mass of chromic oxide, Cr_2O_3. For **bead** test see §**248**.

110. Analysis of the Iron Group (Group III.).

(In absence of Phosphates, etc.)

Boil the filtrate from Group II. in an open dish to expel $\mathbf{H_2S}$, add a few drops of $\mathbf{HNO_3}$, and boil momentarily to oxidize **Fe**$^{\cdot\cdot}$. Immediately add $\mathbf{NH_4Cl}$ and excess $\mathbf{NH_4OH}$. If a precipitate occurs filter and wash, reserving the filtrate for the Zinc Group.

Precipitate: **$Fe(OH)_3$** (brown), **$Cr(OH)_3$** (green), **$Al(OH)_3$** (white).

Dissolve a portion in **HNO_3**, add **$KClO_3$** crystals, and boil to small bulk. Dilute and add **NH_4OH** in slight excess. Filter and wash.		Boil another portion with very dilute **NaOH** solution. Filter.
Precipitate: **$Fe(OH)_3$**. Dissolve in **HCl** and add **KCNS**. A blood-red solution, **$Fe(CNS)_3$**. Test the original solution for $Fe^{\cdot\cdot}$ with **$K_3Fe(CN)_6$**, for $Fe^{\cdot\cdot\cdot}$ with **KCNS** (§99).	Filtrate: **$(NH_4)_2CrO_4$** Acidify with **acetic acid** and add **lead acetate**. A yellow precipitate is **$PbCrO_4$**. 0.002 mg. Cr may be detected in this way. **$Cr(OH)_3$** may also be oxidized to chromate by fusion in the porcelain crucible with **KNO_3** or **$KClO_3$**.	Filtrate: **$NaAlO_2$**. Acidify slightly with **HCl** and add **$(NH_4)_2CO_3$**. Or add to the alkaline solution **NH_4Cl** in excess and boil. A white precipitate is **$Al(OH)_3$**.

111. Notes.—*a.*—Iron is here present, owing to the reducing action of H_2S, as $Fe^{\cdot\cdot}$, which is incompletely precipitated by NH_4OH in the presence of ammonium salt (the ion $NH_4^{\cdot}$). Oxidation to $Fe^{\cdot\cdot\cdot}$ is therefore necessary.

b.—For oxidizing $Fe^{\cdot\cdot}$ but little HNO_3 should be used, and boiling should be brief to avoid oxidation of $Mn^{\cdot\cdot}$ to $Mn^{\cdot\cdot\cdot}$. $Mn^{\cdot\cdot\cdot}$ if present will be precipitated as a brown hydroxide by NH_4OH. $Co^{\cdot\cdot\cdot}$ may also be precipitated with the Iron-Group metals.

c.—A few drops of NaOH solution in 15 to 20 cc. water will dissolve sufficient $Al(OH)_3$ for identification. An excess of NaOH attacks the filter-paper, making filtration difficult and dissolving SiO_2, which is easily mistaken for an Al compound, as it gives a white precipitate with HCl and $(NH_4)_2CO_3$, or with NH_4Cl.

d.—Pb, Sb or Sn, if not previously completely removed, will give reactions similar to those of Al.

e.—$Cr(OH)_3$ is slightly soluble in NH_4OH to a pink solution. It is reprecipitated by boiling off the excess of NH_4OH.

112. Exercises with Ions of the Iron Group.

Obtain the reactions of each kathion and of CrO_4'' separately, following the text and writing equations.

Take a solution of each and identify the metal, following the table at §110 for unknown substances.

Make the following separations: $Al^{\cdots}$ from $Fe^{\cdots}$; $Al^{\cdots}$ from $Cr^{\cdots}$; $Cr^{\cdots}$ from $Fe^{\cdots}$; $Pb^{\cdot\cdot}$ from $Al^{\cdots}$; $Sn^{\cdot\cdot}$ from $Al^{\cdots}$; $Sb^{\cdots}$ from $Cr^{\cdots}$.

Add a drop (1/20 cc.) of N/2 $Al^{\cdots}$ solution to 10 cc. N/2 $FeCl_3$ solution and test for Al, following the table at §110.

Add a drop of N/2 $Cr^{\cdots}$ solution to 10 cc. $FeCl_3$ solution and test for $Cr^{\cdots}$, following the table at §110.

Separate $Cr^{\cdots}$ from $Fe^{\cdots}$ by a method other than that given in the table.

Ascertain the delicacy of the test for $Fe^{\cdot\cdot}$ with $K_3Fe(CN)_6$.

Make pure $FeCl_3$ from metallic iron.

Cobalt.

113. Cobaltous oxide, CoO, is used for coloring glass, the silicate of cobalt formed being deep blue; zaffer is cobalt ore roasted, employed for the same purpose; the blue glass used to absorb yellow sodium light is cobalt glass; smalt is such glass powdered, used as a pigment, cobalt blue. Sympathetic ink, pale pink when cold, blue when warm, is $CoCl_2$ solution. Thenard's blue is a phosphate of Co and Al. Speiss is an impure arsenide of Co and Ni obtained in the process of smelting. Smaltite is arsenide of Co and Ni; cobaltite, CoAsS; copper nickel, NiAs; garnierite, nickel silicate.

114. Cobalt forms an unstable trivalent ion, $Co^{\cdots}$, the solution of whose salts is green in color, and a divalent rose-red ion $Co^{\cdot\cdot}$, whose non-dissociated salts in solution are blue. $CoCl_2$ solution, red when cold, becomes blue on addition of Cl' (HCl or NaCl) or on heating, due in both cases to the formation of non-dissociated salt. Cobalt forms complex ions very readily, those with ammonium in particular being of great variety. The analytical distinctions between Co and Ni depend for the most part upon the fact that Co is more readily oxidized than Ni to the trivalent form and less readily reduced from that form.

115. $Co^{\cdot\cdot}$ is precipitated by soluble **hydroxides** (the **ion OH'**) as blue basic salt, changed by heating to $Co(OH)_2$, rose-red. The precipitate dissolves in NH_4OH or in NH_4Cl.

Sulphides (the **ion S''**) precipitate CoS, black; H_2S causes a slight precipitation in solutions not acidified. The sulphides of Co and Ni are peculiar in that acid which is strong enough completely to prevent their precipitation will not redissolve them after precipitation.*

Carbonate solutions precipitate a mixture of hydroxide and carbonate.

116. Cyanides precipitate $Co(CN)_2$, easily soluble in excess of the reagent, forming a red cobaltocyanide, analogous to the ferrocyanide, but decomposed by acid with precipitation of $Co(CN)_2$: $Co(CN)_2 + 4KCN = K_4Co(CN)_6$.

If but a drop or two of HCl is added and the mixture heated for some time, a colorless cobalticyanide results, analogous to the ferricyanide: $2K_4Co(CN)_6 + 2HCl = 2K_3Co(CN)_6 + H_2 + 2KCl$.

From this solution acids cause no precipitation, a distinction from Ni.

$Co^{\cdot\cdot}$ is slowly oxidized, when warmed with **KNO_2** and **acetic acid**, to a cobaltinitrite, $K_3Co(NO_2)_6$, which separates after long standing in the form of yellow crystals (distinction from Ni).

Cobaltous salt ($Co^{\cdot\cdot}$) warmed with excess of **$NaHCO_3$** (the solid) and **H_2O_2** is oxidized to an unstable soluble green compound, the color being more readily detected after filtration. This is a delicate test (0.02 mg. Co. in 1 cc.), not affected by the presence of Ni.

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* A similar case is the behavior of $Ca_3(PO_4)_2$ toward acetic acid; acetic acid prevents the precipitation of $Ca_3(PO_4)_2$ and yet if the precipitate be produced in neutral mixture and acetic acid then added solution does not take place. This is due to the change of the amorphous modification of $Ca_3(PO_4)_2$, which is first precipitated, to a crystalline form, an amorphous body being always more soluble than the same substance crystalline. It is not known in what way the CoS and NiS become insoluble.

Nitroso-β-naphthol dissolved in 50 per cent acetic acid precipitates a cobaltic compound, brick-red, from Co•• solution, neutral or acidified with HCl or H_2SO_4, a good separation from Ni. The precipitate must be further tested for Co, as the reagent alone may form a precipitate.

117. Cobalt compounds give a blue color to the **borax bead**, a delicate test, masked by much Ni. Heated with Na_2CO_3 on **charcoal** a magnetic mass is obtained (Co_3O_4). Many metallic oxides moistened with $Co(NO_3)_2$ solution and heated take on characteristic colors, useful in their identification before the blowpipe.

Nickel.

118. Nickel is used in the form of an electrolytically deposited coating to protect more readily oxidizable metals; as a constituent of German silver (copper, 100 parts; nickel, 40 parts; zinc, 16 parts) and other alloys used as a foundation for silver-plating. Nickel occurs in nature always associated with cobalt; owing to the similarity of their chemical behavior the two metals are separated with difficulty. In fact the salts of either as ordinarily obtained on the market are not free from traces of the other.

119. Nickel forms the green divalent ion Ni•• and complex ions in considerable variety, those with ammonia being most important.

Soluble **hydroxides** (the **ion OH′**) precipitate $Ni(OH)_2$, pale green, soluble in excess of ammonium hydroxide and also in ammonium salts, forming complex kathions as $Ni(NH_3)_4''$ and $Ni(NH_3)_6''$.

Sulphides and **H_2S** act with Ni as with Co. The precipitated **carbonate** is basic and of green color.

Ni•• treated with a **cyanide**, as directed in §**116** for Co, precipitates as $Ni(CN)_2$, redissolving as $K_2Ni(CN)_4$. On slightly acidulating and digesting hot no oxidation occurs; a little dilute acid now decomposes the nickelocyanide with precipitation of $Ni(CN)_2$ (separation from Co), the precipitate easily redissolving in excess of acid.

120. $Ni^{\cdot\cdot}$ is oxidized by **Cl** or **Br** in alkaline solution to black $Ni(OH)_3$, reducible by **KI** with liberation of iodine. $Co(OH)_3$, similarly precipitated, does not affect KI. This constitutes a very satisfactory test for Ni, even in the presence of large quantities of Co.

121. Ni compounds color the **borax bead** in the oxidizing flame red when hot, yellow-brown when cold. Heated with Na_2CO_3 on **charcoal** metallic Ni is produced, slightly attracted by the magnet.

Manganese.

122. Manganese dioxide, MnO_2, black oxide of manganese, is used as an oxidizing agent, to liberate Cl, Br and I, in manufactures and in sanitary measures; it is employed in glass-making (glass-makers' soap) for removing the green color caused by ferrous compounds; potassium permanganate, $KMnO_4$, a salt dissolving with brilliant purple-red color (Condy's liquid), is of application for its oxidizing power in analysis, in medicine, and for disinfecting purposes; it is deoxidized and its solution decolored by H_2S, H_2SO_3, $H_2C_2O_4$ and other reducing agents. Ferromanganese and spiegeleisen, alloys with iron, are used in steel-making. Borate of manganese is added to varnish to hasten drying. Pyrolusite is MnO_2; psilomelane and wad contain manganese in the same form, with other substances.

123. Manganese forms the pale pink divalent ion $Mn^{\cdot\cdot}$, an unstable ion $Mn^{\cdot\cdot\cdot}$, and two anions having the composition MnO_4, one the green divalent anion of the manganates, stable only in the presence of alkali (the ion OH'), and the other the purple monovalent ion of the permanganates.

124. $Mn^{\cdot\cdot}$ is precipitated by soluble **hydroxides** (the **ion OH'**) as $Mn(OH)_2$, white, becoming brown in air by oxidation. With **NH_4OH** the precipitation is incomplete, as in the case of $Fe^{\cdot\cdot}$, q. v., and when ammonium salt ($NH_4^{\cdot}$) has been added previously does not take place at all.

Sulphides (the **sulphur ion**) precipitate MnS, flesh-colored, soluble even in acetic acid (distinction from ZnS).

Carbonates (the **CO_3 ion**) precipitate $MnCO_3$, white; phosphates precipitate $Mn_3(PO_4)_2$, white.

125. $Mn^{\cdot\cdot}$ is oxidized by **Pb_3O_4 or PbO_2** in the presence of a fairly concentrated non-reducing acid, as HNO_3 or H_2SO_4, to permanganic acid (the ion MnO_4'), purple. Fused with alkali carbonate (or hydroxide) and an **oxidizing agent** any Mn compound forms the bright green manganate (as Na_2MnO_4). These tests are of about equal delicacy.

$$3Mn(OH)_2 + Na_2CO_3 + 4NaNO_3 = 3Na_2MnO_4 + 4NO + CO_2 + 3H_2O$$

$$2Mn(OH)_2 + 5Pb_3O_4 + 30HNO_3 = 2HMnO_4 + 15Pb(NO_3)_2 + 16H_2O$$

126. For **bead** tests see **§248.**

Zinc.

127. Zinc is useful as a constituent of brass and other alloys; galvanized iron is prepared by dipping iron into molten zinc. Zinc oxide, ZnO, zinc white, is used as a paint; the sulphate, crystallizing with $7H_2O$, is white vitriol; the chloride is used as a disinfectant and preservative; the cement used for filling teeth is a mixture of the chloride and oxide.

Sphalerite is black jack, ZnS; smithsonite, $ZnCO_3$; willemite and calamine, silicates; franklinite contains oxides of iron, manganese and zinc.

128. Zinc forms the colorless divalent ion $Zn^{\cdot\cdot}$ and a weak anion, ZnO_2''; there exist also complex ions containing NH_3.

129. Solution of a zinc salt (the ion $Zn^{\cdot\cdot}$) gives a precipitate with soluble **hydroxides** of $Zn(OH)_2$, white, redissolving with excess of the reagent to form in the case of the fixed alkali hydroxides the anion ZnO_2'' and in the case of NH_4OH

certain complex kathions. Hydrolysis of the alkali zincate ($Na_2ZnO_2 + 2H_2O = 2NaOH + H_2ZnO_2$) is increased by heating, which may result in precipitation of the hydroxide. Zinc sulphide, ZnS, white to gray, is precipitated from alkaline or dilute acid solution by the **sulphur ion** of soluble **sulphides** or **hydrosulphuric acid.** **Carbonate** solution precipitates a mixture of hydroxide and carbonate, white, soluble in NH_4OH. **Phosphates** precipitate $ZnHPO_4$, white; **ferrocyanides** $Zn_2Fe(CN)_6$, white, and **ferricyanides** $Zn_3[Fe(CN)_6]_2$, yellowish.

130. Before the blowpipe on **charcoal** with Na_2CO_3 Zn compounds are reduced to the metal, which vaporizes and, undergoing oxidation in the air, settles as a coating of ZnO, yellow when hot and white when cold. This coating, or ZnO from any source, moistened with **$Co(NO_3)_2$** solution and heated takes on a green color.

131. Analysis of the Zinc Group (Group IV.).

Into the ammoniacal solution pass **H_2S**; if a precipitate appears, warm, filter and wash, reserving the filtrate for the following group. Precipitate: **CoS** (black), **NiS** (black), **MnS** (flesh-colored), **ZnS** (white). Treat on the filter with cold dilute (N) **HCl**.

Residue: **CoS, NiS.**		Solution: **$ZnCl_2$, $MnCl_2$, H_2S.**	
For **Co** test in the **borax bead.** If **Ni** is in large excess dissolve the sulphides in **HCl** with a drop of **HNO_3**, precipitate **Co** with nitroso-β naphthol, and test this precipitate in the bead. Or dissolve the sulphides in **HNO_3** and treat with **$NaHCO_3$** and **H_2O_2** (§ 116).	For **Ni** dissolve in **HNO_3**, evaporate excess of acid, treat with **Br** water and **NaOH** and boil, p'p'ting **$Ni(OH)_3$**, black. Wash the precipitate very thoroughly and add to it on the paper hot dilute **KI** solution; acidify the filtrate. If **Ni** is present **I** will be liberated, yellow in water, violet in **CS_2** solution.	Boil to expel **H_2S**. Cool and add **NaOH** in excess. Filter.	
		Precipitate: **$Mn(OH)_2$**. Boil with **Pb_3O_4** and **HNO_3**; let settle. A violet solution, **$HMnO_4$**.	Solution: **Na_2ZnO_2**. Add **H_2S**. A grayish-white precipitate, **ZnS**.

132. Notes.—*a.*—A black precipitate, readily soluble in HCl, is likely to be FeS, not removed in the Iron Group owing to insufficient oxidation. Second Group metals not previously taken out may also precipitate here.

b.—The separation of ZnS from CoS and NiS by treatment with HCl is inexact as acid strong enough to dissolve ZnS will dissolve traces of CoS and NiS, which precipitate as hydroxides with NaOH. The pink color of $Co^{\cdot\cdot}$ must not be mistaken for $HMnO_4$.

c.—The precipitated $Ni(OH)_3$ must be washed with hot water until the washings are perfectly free from alkali (test with litmus-paper), otherwise the liberation of iodine will be prevented.

d.—If H_2S is not expelled before the separation of Zn and Mn, Zn will precipitate as the sulphide instead of dissolving. The alkaline solution must not be heated, as higher temperature increases hydrolysis, precipitating $Zn(OH)_2$.

e.—It is well to wash precipitated sulphides, as in this group, with water containing an electrolyte, as NH_4Cl, which prevents their dissolving as colloids.

f.—The Iron and Zinc Groups are sometimes precipitated together by NH_4OH and $(NH_4)_2S$ in the presence of NH_4Cl. After dissolving all but CoS and NiS in acid, Al and Zn remain in solution on treatment with NaOH; the others precipitate as hydroxides and are identified without separation. As a valuable exercise the learner should draw up a table for analysis of these groups, following this and similar methods.

g.—Insoluble salts, as phosphates, oxalates, etc., of bases of Groups III., IV. and V., held in solution by acid, are precipitated on neutralization of that acid by NH_4OH, as in precipitation of the Iron Group; a special method of precipitating the Iron Group without affecting the later groups is therefore necessary in such cases. Phosphate may be removed by addition of $Fe^{\cdot\cdot\cdot}$ in the presence of acetic acid (formed by adding sodium acetate to the HCl solution), in which all phosphates but those of lead and the Iron Group metals are soluble. The precipitate may contain phosphates of Al and Cr as well as of Fe; Al is separated by dissolving in NaOH; Cr is identified by oxidation to chromate. The filtrate, free from phosphate, may also contain Iron Group metals and is treated in the usual way, beginning with precipitation of Group III. Another method is based on the precipitation of PO_4''' with $Fe^{\cdot\cdot\cdot}$ in the presence of an excess of $BaCO_3$, which, when $Fe^{\cdot\cdot\cdot}$ is in excess, precipitates only the phosphates and hydroxides of Iron-Group metals.

h.—Oxalic acid is destroyed by evaporating to dryness the filtrate from Group II. and heating the residue with strong HNO_3. This treatment drives off HF (which would cause precipitation of CaF_2) and leaves the SiO_2 from silicates as a residue insoluble in acid. Boracic acid is but little precipitated if NH_4Cl is present in large quantity.

133. Exercises with the Ions of the Zinc Group.

Obtain the reactions for each metal separately, following the text and writing equations, and work each as an unknown by the table at §131.

Ascertain the delicacy of the distinctive tests for each metal.

Separate the kathions of this group from one another and $Al^{\cdot\cdot\cdot}$ from $Zn^{\cdot\cdot}$, $Mn^{\cdot\cdot}$ from $Fe^{\cdot\cdot\cdot}$, $Cd^{\cdot\cdot}$ from $Zn^{\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$ from $Co^{\cdot\cdot}$.

Separate $Mn^{\cdot\cdot}$ from $Zn^{\cdot\cdot}$ by precipitation with H_2S in acetic acid solution.

Why not separate $Mn^{\cdot\cdot}$ from $Zn^{\cdot\cdot}$ by precipitation with NH_4OH?

Alkaline Earth Metals (Group V.).

134. This group takes its name from the earthy character of the oxides and the fact that their water solution is alkaline. There is a regular gradation in many of the properties of these metals and of their salts, from barium, with highest atomic weight, through strontium and calcium to magnesium, with lowest atomic weight. They are readily oxidized in the air and, in contrast to metals of preceding groups, form strong bases, barium approaching the alkali-metals in character in this respect, magnesium at the other extreme approaching the earth-metals.

The gradation in solubilities is illustrated by the following compounds:

	Hydroxide.	Sulphate.
Ba	33. grams per liter.	0.0023 grams per liter.
Sr	10.	0.10
Ca	1.25	2.0
Mg	0.01	333.

The sulphates, as salts of a weaker acid, tend to dissolve in HCl and HNO_3; $SrSO_4$ is perceptibly and $CaSO_4$ readily soluble in acid. $BaCrO_4$ has about the same solubility in water as $BaSO_4$; the chromates of the other metals are more soluble. The oxalate of calcium is practically insoluble, the other oxalates sparingly soluble. The phosphates and carbonates are practically insoluble in water, the carbonates dissolving somewhat in NH_4Cl, that of magnesium very readily.

These metals all form divalent ions of fairly strong basic properties. Their salts with strong acids are neutral to litmus in water solution.

Barium.

135. $BaSO_4$ is used as a pigment, baryta white; owing to its high specific gravity (4.5; that of the majority of inorganic salts is between 2 and 3) it is used as an adulterant for increasing weight, as in sizing paper. Oxygen is obtained on the commercial scale by heating BaO_2; $Ba(NO_3)_2$ is used in pyrotechny for producing green light. Barite is heavy spar, $BaSO_4$; witherite, $BaCO_3$.

136. A barium salt (the ion $Ba^{\cdot\cdot}$) in solution not too dilute is precipitated by **fixed alkali hydroxides** as $Ba(OH)_2$, white; **CO_3''** of **carbonates** precipitates $BaCO_3$, white; **sulphates** (**SO_4''**) precipitate $BaSO_4$, white, insoluble in dilute HCl; **chromates** or **dichromates** precipitate $BaCrO_4$, yellow, not readily soluble in acetic acid (distinction from Sr and Ca); **Na_2HPO_4** precipitates $BaHPO_4$, white; **Na_3PO_4** precipitates $Ba_3(PO_4)_2$; **IO_3'** of **iodates** precipitates $Ba(IO_3)_2$, slightly soluble. $BaCl_2$ is insoluble in alcohol (separation from Sr and Ca).

137. Ba compounds (the chloride best, owing to its greater volatility, or other salt moistened with HCl) give the **flame** a green color.

138. A separation of barium from strontium and calcium is based upon the fact that a mixture of soluble sulphate and carbonate changes strontium and calcium sulphates into the carbonates but does not affect barium sulphate.

When an "insoluble" sulphate is treated with a soluble carbonate, as $SrSO_4$ with K_2CO_3, transformation into insoluble carbonate and soluble sulphate ($SrCO_3$ and K_2SO_4) takes place until the SO_4 ions and CO_3 ions are present in the solution in a certain definite ratio; the relative quantity of solid carbonate and sulphate present does not affect the equilibrium. An "insoluble" carbonate in contact with sulphate solution ($SrCO_3$ and K_2SO_4) results in the same equilibrium, transformation thus taking place in either direction.

The equilibrium ratio between the concentration of the SO_4 ions and that of the CO_3 ions is the same as that which is obtained when the "insoluble" carbonate and sulphate are together brought into contact with water; and the relative solubility of the two in the common solution is not unlike their relative solubility in pure water. For calcium the ratio $SO_4'' : CO_3''$ will be large in the equilibrium state, $CaSO_4$ being far more soluble than $CaCO_3$; for the strontium salts this ratio will be smaller and for barium still less.

The sulphates are treated in actual practice with a solution containing three to five parts by weight of K_2SO_4 to one part K_2CO_3. In this mixture the ratio $SO_4'' : CO_3''$ is already greater than that required for equilibrium in the case of the barium compounds, and it does not affect $BaSO_4$, while changing $SrSO_4$ and $CaSO_4$ into the carbonates, which may then be separated from the $BaSO_4$ by dissolving in dilute acid.

Strontium.

139. $Sr(NO_3)_2$ is used for red light in fireworks; Sr forms an insoluble salt with sugar, used in the purification of beet-sugar. Celestite is $SrSO_4$; strontianite, $SrCO_3$.

140. Strontium compounds agree mainly in solubility and precipitations with the corresponding Ba compounds. The chromate and iodate are decidedly more soluble than the same salts of Ba. The dilute solution of **$CaSO_4$** with Sr salts forms a slight precipitate on standing 5 to 10 minutes, HCl preventing the precipitation. This is a distinction from Ca.

Compounds of strontium color the **flame** crimson.

Calcium.

141. Calcium oxide, CaO, lime, quicklime; slaked lime, $Ca(OH)_2$; $CaCO_3$, limestone, marble, chalk, calcite, etc.; $CaSO_4,2H_2O$ is gypsum, land-plaster; this partly dehydrated is plaster of paris; bleaching-powder, chlorinated lime, chloride of lime, is chloride and hypochlorite of calcium, $Ca(OCl)Cl$; $Ca_3(PO_4)_2$, bone-ash, is the mineral constituent of bones; this mixed with carbonaceous matter, as obtained by heating bones, is bone-black; $CaCl_2$ absorbs water, and is used as a drying agent. Fluorspar is CaF_2; dolomite, $CaCO_3.MgCO_3$.

142. Fixed alkali hydroxide (the **OH ion** in considerable concentration) precipitates from solution of calcium salts $Ca(OH)_2$, white; **carbonates** (the **CO_3 ion**) precipitate $CaCO_3$ ("precipitated chalk"), slightly soluble in Na_2CO_3, distinguished from $MgCO_3$ by not dissolving readily in solution of ammonium salts; **Na_2HPO_4** precipitates **$CaHPO_4$**; normal **phosphates** precipitate $Ca_3(PO_4)_2$; **oxalates** (the **ion C_2O_4''**) precipitate CaC_2O_4, practically insoluble in acetic acid, as acetic is a weaker acid than oxalic. $Ca^{\cdot\cdot}$ is but incompletely precipitated by **sulphuric acid** and soluble **sulphates** (the **ion SO_4''**); this serves for its qualitative separation, as the saturated solution of $CaSO_4$ remaining after removal of Ba and Sr as sulphates still gives an abundant precipitate with $(NH_4)_2C_2O_4$. $Ca(NO_3)_2$ is soluble in a mixture of equal volumes absolute alcohol and dry ether, also in amyl alcohol; these are both methods of separation from Sr.

143. Calcium compounds color the flame yellowish red. The carbonate breaks up on heating into CO_2 and CaO, the latter dissolving in water as $Ca(OH)_2$ with alkaline reaction.

Magnesium.

144. Magnesium oxide, MgO, magnesia, magnesia alba, calcined magnesia, a very refractory material used for furnace-linings; $MgSO_4,7H_2O$, epsom salt; dolomite, $CaCO_3$, $MgCO_3$; talc, soapstone, meerschaum are silicates of Mg.

145. $Mg(OH)_2$ is somewhat soluble in water, but with **fixed alkali hydroxide** as precipitant the excess of OH ion decreases the $Mg^{\cdot\cdot}$ concentration to such an extent that precipitation is practically complete. When **NH_4OH** is used some precipitation takes place, but a large proportion of Mg ions must remain in solution, as the OH', the other factor of the solubility-product, is in small quantity. Precipitation with **NH_4OH** fails completely in the presence of ammonium salts, the $NH_4^{\cdot}$ driving back the dissociation of the NH_4OH.

Fixed alkali carbonates (the **ion CO_3''**) precipitate a mixture of $MgCO_3$ and $Mg(OH)_2$, the precipitation being complete on heating; with **$(NH_4)_2CO_3$**, largely hydrolyzed to NH_4OH and H_2CO_3, the precipitation is but partial; ammonium salts increase the hydrolysis and so may entirely prevent precipitation.

Na_2HPO_4 precipitates $MgHPO_4$, in presence of $NH_4^{\cdot}$ and NH_4OH $MgNH_4PO_4$, amorphous at first, at once becoming crystalline (delicacy 0.014 mg. per cc.). Separation of traces of the crystalline precipitate is facilitated by rubbing with a glass rod.

146. Analysis of the Alkaline Earth Group (Group V.). To the filtrate from the preceding group add **NH_4OH** and **$(NH_4)_2CO_3$**, warm and filter. Reserve the filtrate for **Mg** and the alkali-metals.

Precipitate: **$BaCO_3$**, **$SrCO_3$**, **$CaCO_3$** (white).

Dissolve the washed precipitate in a little dilute **acetic acid.**

Solution: **Acetates of Ba, Sr, Ca.**

To a small portion of the solution add **$K_2Cr_2O_7$**; a yellow precipitate is **$BaCrO_4$**, soluble in **HCl**, reprecipitated by dilute **H_2SO_4** as **$BaSO_4$**, white. Apply the flame test. If **Ba** is present add **$K_2Cr_2O_7$** to the entire solution as long as a precipitate is produced, and filter. In the filtrate separate excess of **$K_2Cr_2O_7$** from **$Sr^{\cdot\cdot}$** and **$Ca^{\cdot\cdot}$** by precipitating **$SrCO_3$** and **$CaCO_3$** with **NH_4OH** and **$(NH_4)_2CO_3$**, filtering and redissolving in acetic acid.

Divide the remainder of the solution, or the filtrate from **$BaCrO_4$** freed from **$K_2Cr_2O_7$**, into two portions.

For **Sr**, to one portion add **$CaSO_4$** solution and heat; a slowly-forming precipitate is **$SrSO_4$**. Apply the flame test.	For **Ca**, add to the second portion **K_2SO_4**, precipitating **$SrSO_4$** and possibly **$CaSO_4$**, leaving saturated solution of latter; to the filtrate add **$(NH_4)_2C_2O_4$**, precipitating **CaC_2O_4**, insoluble in **acetic acid**, soluble in **HCl**. Apply the flame test.	For **Mg**, to a portion of the first filtrate add **Na_2HPO_4**. A crystalline precipitate is **$MgNH_4PO_4$**. Test in the remainder of the filtrate for Group VI.

147. Notes.—*a.*—Ammonium salts dissolve alkaline earth carbonates, especially on heating, volatile $(NH_4)_2CO_3$ forming. NH_4OH is added to lessen this tendency.

b.—An excess of acetic acid is to be avoided, for it prevents complete separation of Ba, which then precipitates as the sulphate when the test for Sr is made.

c.—Metals not removed in any of the preceding groups will give a precipitate (not crystalline) when Na_2HPO_4 is added for Mg. To insure complete removal of Ba, Sr and Ca, a drop of $(NH_4)_2SO_4$ and $(NH_4)_2C_2O_4$ solutions may be added before testing for Mg.

148. Exercises on the Alkaline Earth Group.

Obtain the reactions for each kathion as given in the text and analyze a solution of each, treating it as an unknown substance.

Separate the members of the group from one another, using the tables, and also $Ba^{\cdot\cdot}$ from $Pb^{\cdot\cdot}$, $Ca^{\cdot\cdot}$ from $Zn^{\cdot\cdot}$, $Ca^{\cdot\cdot}$ from $Fe^{\cdot\cdot\cdot}$, and $Ba^{\cdot\cdot}$ from $Al^{\cdot\cdot\cdot}$.

Separate the following, not using the methods given in the tables: $Ba^{\cdot\cdot}$ from $Ag^{\cdot}$, $Cu^{\cdot\cdot}$ from $Ba^{\cdot\cdot}$, $Bi^{\cdot\cdot\cdot}$ from $Ca^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$ from $Sr^{\cdot\cdot}$.

Show that the delicacy of precipitation of $Ca^{\cdot\cdot}$ with $(NH_4)_2CO_3$ is lessened by the presence of $NH_4^{\cdot}$.

The Alkali Group (Group VI.).

149. Ammonium. Of rarer occurrence: Lithium.*
Sodium. Rubidium.
Potassium. Caesium.

The metals of this group oxidize rapidly in moist air or water and are kept by immersion in petroleum or benzine or other liquid not containing oxygen: $2K + 2H_2O = 2KOH + H_2$. Gaseous NH_3 dissolves in water to an alkaline solution supposed from analogy to contain NH_4OH, ammonium hydroxide, the radical NH_4 behaving much like an alkali metal. This is the volatile alkali, in distinction to NaOH and KOH, the non-volatile or fixed alkalis.

*** Lithium is an alkali metal forming a sparingly soluble carbonate and an insoluble phosphate. Its compounds impart a bright red color to the flame.**

, precipitate the
$Sb^{\cdots}$, $Hg^{\cdot}$ and $Hg^{\cdot\cdot}$) the oxide o
NH_4OH is in such slight concent
produce the more soluble precipitate
are not affected by NH_4OH, while th
$Mn^{\cdot\cdot}$ and $Fe^{\cdot\cdot}$ is at best incomplet
the presence of $NH_4^{\cdot}$, which decre
NH_4OH. See §20. Other kathion
NH_4OH as the hydroxides, except A
tated as oxides, $Pb^{\cdot\cdot}$, precipitated as
and $Hg^{\cdot\cdot}$, which give mercur-ammoni
fixed alkali hydroxides the precipitates
of six metals, Pb, Sb, Sn, Al, Cr,
ability of the precipitates to take th
forming soluble alkali salts. The pr
solve in NH_4OH in six cases (Ag, C
but here solution is due to the forma
containing ammonia.

151. The alkali metals are in deci
metals of other groups in that most of
soluble in water. The only freely sol
bonates, phosphates and silicates are th
the separation of these metals from o
fact that they are not precipitated

Potassium.

152. In common use are the hydroxide, KOH, caustic potash; K_2CO_3, in an impure form potashes, so called from its occurrence in wood-ash, used for soft soap; pearl-ash is purified K_2CO_3; salt of tartar, a grade of carbonate formerly made by heating potassium bitartrate; KNO_3, niter, saltpeter, used for gunpowder; the chlorate, $KClO_3$, is used in medicine and in match-heads, also in dye-works and as a source of oxygen; KI and KBr are used in medicine and in photography; the bitartrate, $KHC_4H_4O_6$, is cream of tartar; Rochelle salts are the double tartrate of sodium and potassium, $NaKC_4H_4O_6$. The cyanide, KCN, is used in photography, in preparing baths for silvering and gold-plating, and for extracting finely divided gold from its ores. Potassium salts are also used as fertilizers.

153. Potassium forms only the strongly basic monovalent ion $K^{\cdot}$.

154. Except the bitartrate and the platinichloride, potassium salts are soluble in water, the chlorate rather sparingly (ca. 60 grams per liter).

Tartaric acid, $H_2C_4H_4O_6$, or better **sodium acid tartrate, $NaHC_4H_4O_6$,** added to the concentrated solution acidified with acetic acid gives a crystalline precipitate of potassium acid tartrate. The precipitate is made less soluble by addition of alcohol. It is dissolved by alkali hydroxides with formation of the soluble normal tartrate, as $K_2C_4H_4O_6$.

Potassium acid tartrate exhibits a decided tendency to the formation of supersaturated solutions, thereby delaying precipitation. Such a solution is broken up and crystallization caused by shaking, by scratching the test-tube within the liquid with a sharp glass rod, or by introducing a very minute fragment of the crystalline solid.

Hydroplatinichloric acid, obtained by dissolving $PtCl_4$ in HCl, precipitates K_2PtCl_6, yellow, solubility lessened by alcohol.

yellow light-rays of the s
sorbed. It lasts but a moment
small quantity, being less persis
owing to the greater volatility

Sodium.

156. Sodium hydroxide, NaOH
tion lye; the carbonate, Na_2CO_3,
$10H_2O$, sal soda, washing soda;
used for baking are the acid car
with more or less normal carbonat
common salt; the sulphate, cryst
Glauber's salt; sodium nitrate, NaN
peter, the source of HNO_3, extensi
from it the nitrite, $NaNO_2$, is made,
in preparing artificial colors; the
is added to the developer in photogr
tion by air; the thiosulphate, Na_2
hyposulphite, the fixing agent in pho
in solution is water-glass; borax is
crystallization; soap is the sodium
common glass is a silicate of
$NaNH_4HPO_4$ is microcosmic salt, for

157. Sodium fo

ing NH_4OH, hydroxide of ammonium; saturated ammonia water contains ca. 0.5 gram NH_3 to 1 gram H_2O and has a specific gravity of 0.88. Ammonium chloride, NH_4Cl, formerly called muriate of ammonia, hydrochlorate of ammonia, sal ammoniac, a by-product in purification of illuminating gas, is the chief source of ammonia; sal volatile, salt of hartshorn, contains the acid carbonate, NH_4HCO_3, with the carbamate, and is used in medicine.

160. Ammonium forms the weakly basic monovalent ion $NH_4^{\cdot}$ and a wide variety of complex ions with the metals.

161. In solubility the salts resemble those of potassium, ammonium **bitartrate** and ammonium **platinichloride** being obtained as precipitates under conditions similar to those for the corresponding potassium compounds.

Potassium mercuri-iodide (K_2HgI_4) solution containing excess of KOH (**Nessler's reagent**) precipitates ammonia as NHg_2I, brown. The test is so delicate (1-1,000,000) that it is used for estimating the traces of ammonia found in drinking-waters.

An ammonium salt treated with fixed alkali hydroxide, as NaOH, is decomposed in part into NH_4OH, from which NH_3 readily volatilizes and may be recognized by its odor and the formation of a white cloud of NH_4Cl on holding near it a glass rod moistened with HCl. In the solution more NH_4OH is formed to replace that volatilizing. This in turn goes off, more readily on heating, and the ammonium salt may thus be completely decomposed. Other bases do not interfere and the test is made in a portion of the original solution, taken as concentrated as possible owing to the solubility of NH_3 in water. It is advisable to use the solid hydroxide of sodium, potassium or calcium; for traces use a test-tube and boil, passing the gas liberated into dilute Nessler's reagent.

162. Ammonium is capable of **oxidation** to the acid radical NO_3 by strong oxidizing agents. This change occurs to some extent in the atmosphere and in rivers. By reverse change, action of reducing agents, as Zn in KOH solution, produces NH_3 from the radical NO_3.

163. Ammonium compounds are **volatile** below red heat, a distinction from other alkali bases. The only other base whose salts are readily volatilized is mercury.

164. Identification of the Alkali Group (Group VI.).

For NH_4, heat a portion of the original material with concentrated NaOH or solid $Ca(OH)_2$. NH_3 gas is given off, recognizable by its odor, effect on litmus, action with HCl gas, or by Nessler's test.	For K, introduce into the Bunsen flame on the Pt wire a drop of the filtrate from the preceding group; a violet flame, red-violet through the blue glass, indicates K. For tests by precipitation see § 154.	Na is indicated, on applying the flame test, by a yellow color.

165. Notes.—*a.*—Ba, Sr and Ca must be completely removed before making the flame test for K. The color given by these metals seen through the blue glass is very similar to that given by K.

b.—Mg gives a slight yellow flame and interferes also with precipitation tests for the alkali metals. It is removed by $(NH_4)_3PO_4$ or by $Ba(OH)_2$, excess of the latter being taken out with H_2SO_4.

c.—Insignificant traces of Na give a yellow flame of short duration; tests should be made with $Na^{\cdot}$ solutions of known strength to ascertain what intensity of flame indicates $Na^{\cdot}$ in important quantities.

The Chief Acid-Forming Elements in the Periodic System.

Li 7	Be 9.1	**B** 11	**C** 12	**N** 14	O 16	**F** 19	
Na 23	Mg 24.4	Al 27	**Si** 28.4	**P** 31	**S** 32	**Cl** 35.5	
K 39	Ca 40	Sc 44	Ti 48	V 51	Cr 52	Mn 55	Fe 56, Co 59, Ni 58.7
Cu 63.6	Zn 65.4	Ga 70	Ge 72	As 75	Se 79	**Br** 80	
Rb 85.4	Sr 87.6	Y 89	Zr 90.6	Cb 94	Mo 96		Ru 102, Rh 103, Pd 106
Ag 108	Cd 112	In 114	Sn 118.5	Sb 120	Te 127	**I** 126.9	
Cs 133	Ba 137.4	La 138 etc.					
		Yb 173		Ta 183	W 184		Os 191, Ir 193, Pt 195
Au 197	Hg 200	Tl 204	Pb 207	Bi 208			
			Th 232		U 240		

metallic halogen (sa
increase in atomic weight in th
both in power as oxidizers and
with metal and with hydrogen, an
in solubility of similar salts. Eac
the ionic state to the free state
atomic weight: $Cl + HBr = H$
of double decomposition that body
is less soluble or more volatile than
$AgBr + KCl$; $NaCl + HI = HC$
acids, except HF, are among the st

167. Fluorine is a slightly yellowi
stable when in combination as the l
therefore attacks other substances
fluorides.

168. Hydrofluoric acid, obtained
CaF_2, is a colorless gas, readily solu
tion has the properties of a rather w
sociated in normal solution), dissol
Au and Pt (Pb but slightly). It
and brought into contact with the
Owing to its action on glass it is ke
bottles.

The fluorides of the

the gas produced from the material by H_2SO_4. SiF_4 gives with H_2O hydrosilicofluoric acid, H_2SiF_6, forming a barium salt insoluble in water or dilute acids.

169. Chlorine is a heavy greenish-yellow gas, intensely irritating when inhaled. It liquefies easily under pressure of 3.7 atmospheres at 0° and is supplied for use in large quantity in steel cylinders in the liquid state.* Three volumes of chlorine dissolve in one of water, forming chlorine-water; as usual with gases, it is less soluble hot than cold. Next to fluorine the most active of the halegens, chlorine attacks metals, destroys organic tissues and fabrics, and bleaches organic colors. It is obtained by action of oxidizing agents, as MnO_2, HNO_3 or $KClO_3$, on HCl.† $2HCl + O$ (nascent) $= H_2O + Cl_2$.

Free chlorine is identified by its action as an oxidizer and it is therefore essential that other oxidizing agents be absent when the test is made. It bleaches wet litmus-paper and with KI liberates iodine, detected in very small quantity by starch solution or CS_2 (§**186**).‡

170. The chief acids containing chlorine are:

Hydrochloric acid, HCl, forming chlorides.

Chloric acid, $HClO_3$, forming chlorates.

Hypochlorous acid, HClO, forming hypochlorites.

It forms also chlorous acid, $HClO_2$, and perchloric acid, $HClO_4$.

Hydrochloric Acid and the Chlorides.

171. Hydrochloric acid, muriatic acid, is a colorless suffocating gas soluble in about twice its weight (1/450 its volume) of water; a 20 per cent solution has the maximum boiling-point, 110°, and on heating stronger or weaker solutions either HCl or H_2O in excess is distilled off, leaving the 20 are scarcely

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* Thoroughly dried chlorine does not attack metals; it is a curious fact that very many chemical changes take place only in the presence of moisture.

† Make chlorine by these methods and identify it.

‡ Further upon the reactions of chlorine as an oxidizing agent, Prescott and Johnson's Qual. Anal., 1901, p. 328.

172. The gas, obtained by mean
from the solid chloride, is identifie
of **AgNO$_3$** solution on the glass rod,
precipitate of AgCl, insoluble in H
(distinction from iodide), reprecipit
tion with HNO$_3$: HCl + AgNO$_3$ =
2NH$_4$OH = (NH$_3$)$_2$AgCl + 2H$_2$O;
= AgCl + 2NH$_4$NO$_3$.

A drop of **NH$_4$OH** solution on t
with HCl gas, gives a white cloud of
acids react similarly.

The Cl ion, contained in water
acid and its salts, is precipitated b
Group, **Ag$^{\cdot}$**, **Pb$^{\cdot\cdot}$** and **Hg$^{\cdot}$**, form
PbCl$_2$ and HgCl. It is convenientl
tion with **AgNO$_3$**, the precipitate be
soluble in NH$_4$OH, reprecipitated
of hydrobromic acid and bromides
the same way and where the two ar
tested for by one of the following m

Digest the mixed AgCl and AgBr
carbonate, which dissolves AgCl m
AgBr, and precipitate AgCl from th
HNO$_3$; or obtain the material und
solid state and distill it with concen

acetate as $PbCrO_4$, is evidence of Cl' in the original material. The limit of delicacy in the presence of Br' is about 2 mg. Cl'.

Hydrobromic acid or bromides (the ion Br') if present form no corresponding chromium compound, but are oxidized to free Br, which may go into the distillate and give a white precipitate of $PbBr_2$ on addition of lead acetate.

AgCl is not decomposed by acids; HgCl is slowly changed to soluble mercuric salts by HNO_3.

173. In analysis of insoluble chlorides they are fused with Na_2CO_3, after which extraction with water gives the Cl ion in solution as NaCl. The thoroughly washed residue is dissolved in HNO_3 and tested for bases. The following equations represent this class of changes:

$2AgCl + Na_2CO_3 = 2Ag + 2NaCl + O + CO_2$
$2HgCl + Na_2CO_3 = 2Hg\ (\text{vaporized}) + 2NaCl + O + CO_2$
$PbCl_2 + Na_2CO_3 = PbO + 2NaCl + CO_2$

The chlorides are as a class more **volatile** than other salts.

Hypochlorous Acid and its Salts.

174. Bleaching-powder, called also chloride of lime or chlorinated lime, is probably a double salt, a hypochlorite and chloride of calcium, $CaCl(OCl)$; it is in extensive use, owing to the readiness with which it gives up chlorine, for bleaching cloth, paper and other fabrics, and as a disinfectant. It is prepared by treating slaked lime ($Ca(OH)_2$) with chlorine. The corresponding sodium compound gives the "solution of chlorinated soda." Eau de Javelle contains the potassium compound.

175. Hypochlorous acid, owing to its instability, has not been obtained except in water solution. Hypochlorites are formed by treating metallic hydroxides with chlorine in the cold; they go over into chlorates slowly when cold, more rapidly when hot and in presence of excess of chlorine: $2NaOH + 2Cl = NaCl + NaOCl + H_2O$; $3NaOCl = NaClO_3 + 2NaCl$.

The hypochlorites are strong oxidizing agents; they all readily give up chlorine on treatment with acid, even the CO_2 of the air effecting this reaction: $CaCl(OCl) + CO_2 = CaCO_3 + Cl_2$.

176. Hypochlorites are all soluble in water. **$AgNO_3$** with $NaClO$ gives: $3AgNO_3 + 3NaClO = 2AgCl + AgClO_3 + 3NaNO_3$.

Chloric Acid and Chlorates.

177. Chloric acid, $HClO_3$, decomposes spontaneously and has not been obtained in greater concentration than 20 per cent water solution. The chlorates are quite stable. $KClO_3$ is in common use in medicine and is also used as a powerful oxidizer in explosives, match-heads and fireworks. Oxygen is prepared from it by heating. It is the least soluble of the chlorates, 60 grams dissolving in one liter.* $KClO_3$ heated or rubbed with oxidizable substances gives up its oxygen explosively. It should be pulverized by itself, in small quantity at first to insure absence of organic matter; if combustible material is to be mixed with it, care should be exercised to avoid pressure or concussion.

Chlorates are formed by action of excess of chlorine with heat on metallic hydroxides. This is done at present on the large scale by electrolytic methods:

$$6Ca(OH)_2 + 12Cl = 5CaCl_2 + Ca(ClO_3)_2 + 6H_2O$$
$$6KOH + 6Cl = 5KCl + KClO_3 + 3H_2O$$

178. A small fragment of chlorate cautiously warmed with concentrated **H_2SO_4** decomposes with sharp detonation, becoming a violent explosion with larger quantities. It is further identified by **reduction** to chloride either by **heating** (on Pt foil) or by action of **Zn** or **H_2SO_3**. (A precipitate of Ag_2SO_3, soluble in HNO_3, must not be mistaken for AgCl.) $KClO_3 + 3H_2SO_3 = KCl + 3H_2SO_4$; $3Zn + KClO_3 + 3H_2SO_4 = KCl + 3ZnSO_4 + 3H_2O$; $KClO_3 = KCl + 3O$.

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* There are four common acids whose normal salts are all soluble in water—nitric, chloric, acetic, and hypochlorous.

$KClO_3$ oxidizes HCl, liberating chlorine, a convenient method of preparation of the latter in small quantities: $KClO_3 + 6HCl = KCl + 6Cl + 3H_2O$.

Bromine.

179. Bromine under ordinary conditions is a very volatile brown liquid, sp. gr. 3.1, boiling at 60° with formation of a brown-red vapor which resembles chlorine in its properties, although less active. It dissolves in water, 3 grams in 100 cc. (bromine-water); it is more soluble in solutions of bromides and other salts, forming unstable anions, as Br_3', etc., and in alcohol, ether, chloroform and carbon disulphide, the solutions having an orange-yellow to brownish-yellow color. It colors starch yellow.

Bromine dissolves colorless in excess of alkali hydroxide solution, forming bromide with hypobromite and bromate, the first step in the manufacture of alkali bromides: $2Br + 2KOH = KBr + KBrO + H_2O$; $6Br + 6KOH = 5KBr + KBrO_3 + 3H_2O$.

Hypobromite is formed in the cold, bromate in hot solution with excess of bromine.

Bromine is prepared by the action of oxidizers on the Br ion of bromides. This reaction takes place more readily than the corresponding change of the Cl ion to free chlorine, and not only those oxidizers which liberate chlorine but also others less energetic may be used, as chlorine itself or concentrated H_2SO_4. HBr is thus a reducing agent, more readily decomposed with liberation of halogen than HCl, less readily than HI.

180. Bromine forms:

Hydrobromic acid, HBr.

Hypobromous acid, HBrO.

Bromic acid, $HBrO_3$.

Hydrobromic Acid and its Salts.

181. Hydrobromic acid is a gas, less stable than HCl, which it resembles. It dissolves to 80 per cent in water at

182. Bromine combined as h
(the Br ion) is identified by
with **Cl-water** added to the acid
is necessary in the latter case.
with the solution dissolve the
as a yellow or brown globule.*
the CS_2 greenish-yellow, at the
owing to separation of sulphur.
acid or an iodide, that is, of the
first be liberated on treatment
color (violet) in CS_2 will mask t
of the iodine it may be oxidized
of excess of chlorine-water adde
unaffected; or by means of satu
dilute H_2SO_4 (heat but do not
$KI + KClO_3 = KCl + KIO_3$.
a little of the solution at interval
ascertain if iodine is completely o

The bromine of dissolved bromi
lead salts (the **ion Pb$^{\cdot\cdot}$**) as PbI
water than $PbCl_2$; by **silver** salt
insoluble in dilute HNO_3, less

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* Where a substance is soluble in each of
in H_2O and CS_2, it distributes itself betw
definite ratio exists between

AgCl; by **mercurous** salts (the **ion** $\mathbf{Hg^{\cdot}}$) as HgBr, yellowish white.

Iodine.

183. Iodine is prepared from the iodates occurring with Chile saltpeter ($NaNO_3$) and from the iodides of kelp or seaweed ash. Tincture of iodine is a solution in alcohol, compound liquor a solution in KI.

It is obtained in lustrous iron-gray scales which volatilize without melting (sublime) unless under the pressure of iodine vapor; the vapor is of a bright violet color. Iodine is slightly soluble in water, much more abundantly in presence of the I ion, with which it combines loosely to form such monovalent anions as I_3'. It dissolves readily in alcohol, ether, carbon disulphide and glycerine. In cold dilute water solution it colors starch intensely blue, a very delicate reaction.

With alkali hydroxides it forms colorless iodide and hypoiodite, rapidly changing to iodate: $2I + 2KOH = KI + KIO + H_2O$; $3KIO = 2KI + KIO_3$. The so-called colorless tinctures of iodine are made in this way or with reducing agents which form the iodide ion, as: $Na_2SO_3 + 2I + H_2O = Na_2SO_4 + 2HI$; $2I + H_2S = 2HI + S$ (used for preparing HI in small quantity). The solution of iodine in NH_4OH deposits a dark-brown powder, iodide of nitrogen, $N_2H_3I_3$, violently explosive when dry. The blue starch color is destroyed by these reagents.

184. The most important acids containing iodine are:

Hydriodic, HI, forming iodides.

Iodic, HIO_3, forming iodates.

Hydriodic Acid and the Iodides.

185. Hydriodic acid, HI, is a gas, less stable than either HCl or HBr; the saturated water solution at 0° contains 90 per cent HI. Iodides of potassium, ammonium, arsenic, sulphur and phosphorus are pharmacopœial preparations.

oxidizes in air, with

186. The iodine ion of iodid free iodine, perhaps most sati in acid solution. The free io with **CS_2**, which dissolves it wi of a little **starch** solution.* C an excess of chlorine, as it decol $I + 5Cl + 3H_2O = HIO_3 +$ **HNO_3**, **MnO_2**, **chromates**, **pern** and **ferric** salts may be used— acid ($H^{\cdot}$). When iodine is liber tion it may appear as a black pr

The iodine of iodides (I') is p yellow, by **$Ag^{\cdot}$** as AgI, yellowish, (separation from $AgCl$); by **$Hg^{\cdot}$** to Hg and HgI_2; by **$Hg^{\cdot\cdot}$** as Hg iodide (I') to form the anion Hg by **$Cu^{\cdot\cdot}$** as CuI mixed with free

Iodic Acid and

187. Iodic acid is a white, crys freely soluble in water. Iodates manufacture of iodides (from I a incompletely removed, remaining

188. Iodates in water solution is precipitated by $Ba^{\cdot\cdot}$

metals only are freely soluble in water—a marked distinction from chlorates and bromates. KIO_3 is insoluble in alcohol (separation from KI).

189. Reducing agents liberate iodine from iodic acid, taking it up again when used in excess: $2HIO_3 + 5H_2SO_3 = 2I + 5H_2SO_4 + H_2O$; $2I + H_2SO_3 + H_2O = 2HI + H_2SO_4$. This constitutes a delicate test for iodic acid. The presence of iodate in KI is shown by the immediate separation of iodine on adding a dilute acid not an oxidizing agent, as tartaric or oxalic: $5HI + HIO_3 = 6I + 3H_2O$.

Nitrogen.

190. Compounds of nitrogen of interest here are:
Ammonia, NH_3, forming ammonium salts.
Nitric acid, HNO_3, forming nitrates.
Nitrous acid, HNO_2, forming nitrites.
Cyanogen, C_2N_2, forming cyanides, etc.

Nitric Acid and Nitrates.

191. Absolute nitric acid, HNO_3, is liquid, of sp. gr. 1.56, boiling point 86°, very difficult to preserve without some decomposition. Fuming nitric acid is of sp. gr. ca. 1.50. The constant boiling mixture contains 68 per cent acid and boils at 120°. Aqua fortis is an old name. Chile saltpeter, Peruvian niter, $NaNO_3$, is used as a source of nitric acid, also for the manufacture of KNO_3 by transposition with KCl. Niter, India saltpeter, is KNO_3, formed by slow oxidation of organic substances containing nitrogen. Gunpowder is a mixture of KNO_3, sulphur and charcoal. Nitric acid is used for making other explosives, as nitro-glycerine, guncotton, etc.; gun-cotton (nitro-cellulose) is the basis of the modern smokeless powder; dynamite is a porous earth impregnated with nitro-glycerine; nitro-gelatine is a solution of gun-cotton in nitro-glycerine; collodion is an alcohol-ether solution of a substance having about the same composition as nitro-cellulose. Aniline, the basis of a number of coal-tar

readiness to oxidizable substan
same precautions must be tak
with reducing agents as in the
dangerous explosions may result

193. The usual product of r
changing to brown NO_2 in the a
are treated with HNO_3. NO dis
brown kathion $FeNO^{\cdot\cdot}$: $FeSO_4$
the brown-ring test $FeSO_4$ solut
the test-tube is well mixed with
solution to be tested and concentr
down the side of the tube in suc
layer under the $FeSO_4$. Cool an
shake; in the presence of nitrate
between the two layers of liquid.
the HNO_3 to NO, which dissolves
the solution having a brown color.
ates and iodates interfere with th
color: $6FeSO_4 + 2HNO_3 + 3H_2SO_4$
$4H_2O$.

A number of tests depend upon
an oxidizer and are to be used on
other oxidizers is assured. A solutic
decolored on warming with HCl in th
A drop of a sulphuric acid solut
$(C_6H_5)_2NH$ in

conveniently with **Al** wire in the presence of fixed alkali hydroxide, the gas liberated being passed into Nessler's reagent. Owing to the extreme delicacy of this test for ammonia blank experiments should be carried out to insure purity of reagents.

Nitrous Acid and Nitrites.

194. Nitrous acid, HNO_2, has not been prepared pure; even in dilute solution it decomposes rapidly. Potassium nitrite, long the salt most commonly in use, has of late been replaced by the cheaper sodium compound, q. v. The acid is weak and its salts have alkaline reaction in water. Nitrites are sometimes present as impurities in commercial nitrates, forming if the nitrate is too strongly heated in preparation: $KNO_3 + \text{heat} = KNO_2 + O$.

195. Nitrites are all soluble in water, $AgNO_2$ somewhat sparingly soluble (8 grams per liter).

196. Nitrites act both as oxidizing and as reducing agents, NO resulting in the former case (with **KI**, etc.) and HNO_3 in the latter (with $\mathbf{K_2Cr_2O_7}$, $\mathbf{KMnO_4}$, etc.). **Al** in KOH reduces nitrite to NH_3.

Nitrous acid by spontaneous decomposition forms HNO_3 and NO, brown on contact with air. This reaction, produced by adding dilute **sulphuric** or **acetic acid** to the solid nitrite or concentrated solution, serves as a method of identification: $3HNO_2 = HNO_3 + 2NO + H_2O$.

In the brown-ring test nitrites give the same result as nitrates. If acetic acid be substituted for sulphuric in this test the brown ring is obtained with nitrites but not with nitrates.

Nitrites acidulated with acetic acid or very dilute sulphuric acid instantly liberate iodine from **KI**, a delicate test, distinguishing nitrites from nitrates.

197. Cyanogen (C_2N_2, formerly written Cy), formed by heating $Hg(CN)_2$, by treating cupric salts ($Cu^{\cdot\cdot}$) in solution with KCN (CN'), or directly from C and N at high temperatures, is a poisonous gas, soluble in water. The following are some of the acids in which the group CN occurs:

Hydrocyanic acid, HCN, forming cyanides.
Hydroferrocyanic acid, $H_4Fe(CN)_6$, forming ferrocyanides.
Hydroferricyanic acid, $H_3Fe(CN)_6$, forming ferricyanides.
Sulphocyanic acid, $HCNS$, forming sulphocyanates.

Hydrocyanic Acid and Cyanides.

198. Hydrocyanic acid, HCN, prussic acid, is a colorless liquid, boiling at 27°, soluble in water in all proportions; the solution used in medicine contains 2 per cent acid. Oil of bitter almonds frequently contains HCN; KCN is used in photography as a fixing agent, to dissolve silver salts, also in large quantities in the cyanide process of extracting gold from its ores. KCN is made on a large scale by heating $K_4Fe(CN)_6$ with iron.

Hydrocyanic is a very weak acid, dissociated in N/10 solution to only 0.011 per cent, and its soluble salts, as KCN, are hydrolyzed with formation of non-dissociated HCN, detectable by its odor, and KOH, which gives the solution alkaline reaction. It is a deadly poison in solution or as vapor. Potassium cyanide is intensely poisonous, as are all compounds whose water solution contains the ion CN'.

199. Cyanides of alkali-metals, alkaline-earth metals and $Hg(CN)_2$ are soluble in water, the others insoluble. **Silver** salts (**$Ag^\cdot$**) precipitate $AgCN$, resembling $AgCl$, insoluble in HNO_3, soluble in NH_4OH; the precipitation does not take place from solution of $Hg(CN)_2$, which is but little dissociated. Soluble cyanides contain the hydroxyl ion in sufficient concentration to precipitate the hydroxides of a number of the metals.

Many of the precipitated cyanides dissolve in presence of excess of soluble cyanide (the ion CN'), with formation of complex anions of various degrees of stability. Some, as $Ni(CN)_4''$, formed by treating precipitated **$Ni(CN)_2$** with

KCN, are broken up by mineral acid, HCN being liberated: $Ni(CN)_2 + 2KCN = K_2Ni(CN)_4$; $K_2Ni(CN)_4 + 4HCl = NiCl_2 + 2KCl + 4HCN$. Others are more permanent: **$Fe(CN)_2$**, precipitated, dissolves in CN', forming $Fe(CN)_6''''$, stable in presence of acid or alkali ($H^{\cdot}$ or OH'). Addition of dilute acid gives $H_4Fe(CN)_6$, hydroferrocyanic acid, forming salts with most bases. Co, Mn and Cr form such stable complex anions

HCN is recognized by its **odor** or by transformation into $Fe(CNS)_3$ or $Fe_4[Fe(CN)_6]_3$. For $Fe(CNS)_3$, add to the material, in an evaporating dish, a few drops of yellow **ammonium sulphide** and warm till colorless and free from sulphide; filter out any residue or precipitate. Slightly acidulate with HCl (which should not liberate H_2S) and add a drop of **$FeCl_3$** solution, producing, if CN' was present, a blood-red solution of $Fe(CNS)_3$. To form ferrocyanide add to another portion **KOH** and **$FeSO_4$**, warm a short time, acidulate, and add **$FeCl_3$**, precipitating blue $Fe_4[Fe(CN)_6]_3$.

200. AgCN **heated** does not fuse but forms metallic Ag, soluble in HNO_3 (distinction from AgCl).

Hydroferrocyanic Acid and its Salts.

201. Potassium ferrocyanide is yellow prussiate of potash; ferric ferrocyanide, $Fe_4[Fe(CN)_6]_3$, is prussian blue.

202. The ferrocyanides of the alkali-metals and alkaline-earth metals are soluble in water (that of barium sparingly); those of the other metals are insoluble in water. The following are some of the precipitations caused by $K_4Fe(CN)_6$:

$Bi^{\cdot\cdot\cdot}$ gives $Bi_4[Fe(CN)_6]_3$, white;
$Cd^{\cdot\cdot}$ gives $Cd_2Fe(CN)_6$, white;
$Cu^{\cdot\cdot}$ gives $Cu_2Fe(CN)_6$, red-brown;
$Fe^{\cdot\cdot}$ gives $K_2FeFe(CN)_6$, whitish blue;
$Fe^{\cdot\cdot\cdot}$ gives $Fe_4[Fe(CN)_6]_3$, prussian blue;
$Pb^{\cdot\cdot}$ gives $Pb_2Fe(CN)_6$, white;
$Mn^{\cdot\cdot}$ gives $Mn_2Fe(CN)_6$, white, soluble in HCl;
$Ag^{\cdot}$ gives $Ag_4Fe(CN)_6$, white;
$Zn^{\cdot\cdot}$ gives $Zn_2Fe(CN)_6$, white, gelatinous.

The precipitates are decomposed by OH' owing to the fact that the metallic hydroxides are less soluble than the ferrocyanides; they are not affected by dilute $H^{\cdot}$: $Fe_4[Fe(CN)_6]_3 + 12KOH = 4Fe(OH)_3 + 3K_4Fe(CN)_6$.

$K_4Fe(CN)_6$ with concentrated $\mathbf{H_2SO_4}$ liberates HCN: $2K_4Fe(CN)_6 + 3H_2SO_4 = 3K_2SO_4 + K_2FeFe(CN)_6 + 6HCN$.

Hydroferricyanic Acid and its Salts.

203. The anion of this acid is identical in composition with that of the preceding; it is trivalent in this case where before it was tetravalent. The properties of the two are quite unlike.

Red prussiate of potash is $K_3Fe(CN)_6$; it is made by the action of chlorine or other oxidizing agent on ferrocyanide: $K_4Fe(CN)_6 + Cl = K_3Fe(CN)_6 + KCl$; reducing agents effect the reverse change.

204. The ferricyanides are mostly insoluble or sparingly soluble in water, except those of the alkali and alkaline-earth metals. The following are some of the precipitates obtained:

$\mathbf{Bi}^{\cdot\cdot\cdot}$ gives $BiFe(CN)_6$, light brown;
$\mathbf{Cu}^{\cdot\cdot}$ gives $Cu_3[Fe(CN)_6]_2$, yellow-green;
$\mathbf{Fe}^{\cdot\cdot}$ gives $Fe_3[Fe(CN)_6]_2$, Turnbull's blue;
$\mathbf{Fe}^{\cdot\cdot\cdot}$ gives no precipitate, greenish solution;
$\mathbf{Pb}^{\cdot\cdot}$ gives no precipitate unless concentrated;
$\mathbf{Mn}^{\cdot\cdot}$ gives $Mn_3[Fe(CN)_6]_2$, brown;
$\mathbf{Ag}^{\cdot}$ gives $Ag_3Fe(CN)_6$, red-brown;
$\mathbf{Zn}^{\cdot\cdot}$ gives $Zn_3[Fe(CN)_6]_2$, orange.

These precipitates are decomposed by OH' but are formed in neutral or acid solutions.

$K_3Fe(CN)_6$ is soluble in **alcohol**, a separation from $K_4Fe(CN)_6$.*

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* The complex ions formed by $Fe^{\cdot\cdot}$ and $Fe^{\cdot\cdot\cdot}$ with CN' are among the most stable known, the secondary dissociation into $Fe^{\cdot\cdot}$ or $Fe^{\cdot\cdot\cdot}$ and CN' being so slight that the ordinary reactions for the simple ions fail. The fact that all iron compounds dissolve in KCN solution shows that the iron ions are present

Sulphocyanic Acid and its Salts.

205. Sulphur melted with a cyanide or boiled with its solution forms a sulphocyanate, as KCNS. Sulphocyanic acid, HCNS (also called thiocyanic), resembles HCl in activity and in the solubilities of its silver salt, which is unaffected by hot dilute HNO_3 but is soluble in NH_4OH. Mercurous salts (the ion $Hg^{\cdot}$) precipitate HgCNS, white, which increases decidedly in volume on heating (Pharaoh's serpents). The characteristic reaction of CNS′, the anion contained in solutions of sulphocyanic acid and sulphocyanates, is the formation with **$Fe^{\cdot\cdot\cdot}$** of the blood-red $Fe(CNS)_3$, soluble in ether, decomposed by $HgCl_2$ with formation of colorless $Hg(CNS)_2$; the color is more intense in the presence of acid, as HCl, which prevents hydrolysis into $Fe(OH)_3$ and HCNS.

HNO_3 and other **oxidizers** give a red color with KCNS; in excess they destroy the color of $Fe(CNS)_3$.

Alkali hydroxide (OH′) decomposes sulphocyanates owing to the slighter solubility of the hydroxides of the metals; **$H^{\cdot}$** does not affect them.

Carbonic Acid and Carbonates.

206. Carbon dioxide dissolves in about its own volume of water,* giving a solution of faintly acid reaction from which, on addition of a base, salts corresponding to an acid H_2CO_3 may be obtained. The anhydride, CO_2, is exhaled in the

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in the resulting complexes in less concentration than in a saturated water solution of the least soluble iron compound (see § 16); and the further fact that these bodies are not poisonous indicates absence of the CN ion. In contrast to such complexes are the double salts like the alums, which are almost completely split up into their components on dissolving and which therefore give the primary ion reactions. Some complexes, as $KAg(CN)_2$, from which $Ag^{\cdot}$ is precipitated by H_2S, not by HCl, lie between these two extremes and give only the more delicate tests for the simple ions.

* The mass of a gas which will dissolve in a liquid is in general proportional to the pressure to which the gas is subjected. This is Henry's Law. CO_2 under a pressure of two atmospheres is twice as soluble in water as CO_2 under a pressure of one atmosphere. As in the case of the saturated solution of a solid, for equilibrium a fixed ratio must exist between the concentration in the one phase and the concentration in the other phase.

breath, is formed in common combustion and in fermentation, and constitutes the small proportion of the atmosphere from which plants obtain their carbon.

The normal sodium carbonate, Na_2CO_3, $10H_2O$, is known as soda, washing soda, sal soda; the bicarbonate, $NaHCO_3$, is baking-soda or saleratus; soda-water is water saturated under pressure with CO_2, obtained by action of dilute H_2SO_4 on limestone or as a by-product of fermentation processes; the effervescence of natural waters and of beverages is due to escaping CO_2.

207. The only carbonates soluble in water are those of ammonium, sodium and potassium, and solutions of these cause precipitation of all other bases. The soluble carbonates undergo hydrolysis, and even the acid carbonates of sodium, potassium and ammonium have alkaline reaction in water. The precipitated carbonates are likewise hydrolyzed, and those of the more weakly basic metals contain a mixture of hydroxide and carbonate, the proportion of hydroxide being greater the more dilute the solution and the higher the temperature; with the **stronger bases** the precipitate is the normal carbonate, with $\mathbf{Sn}^{\cdot\cdot}$, $\mathbf{Al}^{\cdot\cdot\cdot}$, $\mathbf{Cr}^{\cdot\cdot\cdot}$ and $\mathbf{Fe}^{\cdot\cdot\cdot}$ it is chiefly the hydroxide, with $\mathbf{Sb}^{\cdot\cdot\cdot}$ the oxide; **antimonic** and **stannic** compounds are precipitated as H_3SbO_4 and H_2SnO_3 respectively. Carbonic acid is but little dissociated and does not contain CO_3 ions in sufficient concentration to reach the solubility-product of the metallic carbonates, hence it does not cause precipitation.

On treatment with a less volatile **acid** than carbonic, carbonates give up CO_2 with effervescence. $\mathbf{H_2SO_4}$ for use in this test should be diluted, as concentrated H_2SO_4 liberates CO_2 from oxalates. The gas passed into $\mathbf{Ca(OH)_2}$ solution precipitates $CaCO_3$, white, redissolving in excess of CO_2 with formation of an acid carbonate. Breathing through a tube into the reagent produces the same effect.

208. Acid carbonates are decomposed by **heat**, even in solution, CO_2 being given off. Carbonates of all **metals**

except those most strongly basic (the alkali-metals and barium) are decomposed by heat, CO_2 being liberated: $CaCO_3 = CaO + CO_2$.

Oxalic Acid and Oxalates.

209. Oxalic acid is an acid of moderate strength obtained as the crystalline $H_2C_2O_4{,}2H_2O$ by oxidation of sawdust or other organic matter with HNO_3. Sodium and potassium oxalates are obtained by fusing the hydroxides of those metals with sawdust. KHC_2O_4 is the sour substance in oxalis; $K_2Fe(C_2O_4)_2$ is used as a developer for AgBr plates.

210. Oxalates and oxalic acid in water solution contain the ion C_2O_4'', which causes precipitation from solutions of **all salts** except those of $\mathbf{NH_4^{\cdot}}$, $\mathbf{Na^{\cdot}}$, $\mathbf{K^{\cdot}}$, $\mathbf{Mg^{\cdot\cdot}}$, $\mathbf{Cr^{\cdot\cdot\cdot}}$, $\mathbf{Fe^{\cdot\cdot}}$, $\mathbf{Fe^{\cdot\cdot\cdot}}$, $\mathbf{Al^{\cdot\cdot\cdot}}$, $\mathbf{Sn^{\cdot\cdot\cdot\cdot}}$. Precipitation of $\mathbf{CaC_2O_4}$ is most used in analysis. The precipitates are soluble in acids stronger than oxalic, as HCl, and but little soluble in weaker acids, as acetic. Many of the oxalates react with excess of alkali oxalate to form soluble double oxalate.

211. Oxalic acid is a reducing agent, undergoing change to CO_2. In this way it precipitates **Au** from solution and decolors acidulated solution of **permanganate.** The latter reaction is used as a means of identification, the gas being passed into $\mathbf{Ca(OH)_2}$ solution; carbonates, of course, first must be decomposed by boiling with dilute H_2SO_4: $2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 = 2MnSO_4 + 10CO_2 + K_2SO_4 + 8H_2O$.

Concentrated $\mathbf{H_2SO_4}$ takes up water, causing the following change: $H_2C_2O_4 = H_2O + CO_2 + CO$.

212. On **heating,** oxalates become carbonates with liberation of CO. At higher temperatures the changes peculiar to carbonates take place (§**208**). Silver oxalate, when heated, decomposes with a slight explosion.

Acetic Acid and Acetates.

213. Acetic acid, $HC_2H_3O_2$, is a solid (glacial acetic acid), melting at 17.5°, readily soluble in water; the solution is referred to ordinarily as acetic acid. Vinegar owes its sour taste and odor to a content of 4 to 5 per cent of acetic acid; sugar of lead is basic lead acetate; the true verdigris, used as a pigment, is a basic acetate of copper.

214. The acetates are all soluble in water, mercurous acetate and silver acetate sparingly soluble. Ferric salts with acetates in neutral solution give a red liquid. Ferric acetate undergoes far-reaching hydrolysis, and the color is due to $Fe(OH)_3$ which remains dissolved in the colloid form. The color is destroyed by acids, not by $HgCl_2$ (distinctions from sulphocyanate). Heat increases the hydrolysis and slowly precipitates $Fe(OH)_3$ containing some ferric acetate.

Less volatile acids liberate from acetates acetic acid, recognizable by its odor; an acetate warmed with H_2SO_4 and alcohol forms ethyl acetate, acetic ether, $C_2H_5C_2H_3O_2$, of peculiar, agreeable odor.

Sulphur.

215. Sulphur is readily recognized by the odor and other properties of the sulphur dioxide which it forms on burning. Sulphur is soluble in CS_2 and in hot alkali hydroxide solutions, in the latter case owing to chemical combination. It is slowly oxidized by HNO_3 or Cl to H_2SO_4. In the ordinary form it is yellow; freshly precipitated it is white. Roll-sulphur or brimstone is obtained by casting molten sulphur into sticks; sublimed sulphur, flowers of sulphur, by condensing the vapor directly to the solid; milk of sulphur results on precipitating polysulphides of calcium, CaS_4 or CaS_5, with acid.

216. The following are among the more important acids formed by sulphur:

Hydrosulphuric acid, H_2S, forming sulphides.
Thiosulphuric acid, $H_2S_2O_3$, forming thiosulphates.
Sulphurous acid, H_2SO_3, forming sulphites.
Sulphuric acid, H_2SO_4, forming sulphates.

Hydrosulphuric Acid and the Sulphides.

217. Hydrosulphuric acid, H_2S, is at ordinary temperature and pressure a gas soluble in three times its volume of water; the saturated solution is about N/6 and has very weak acid properties. The soluble salts, as $(NH_4)_2S$, are hydrolyzed in water, having alkaline reaction and H_2S odor. The polysulphides of alkali and alkaline earth metals form by addition of S to a sulphide. Yellow ammonium sulphide is a polysulphide, $(NH_4)_2S_x$; liver of sulphur is a mixture of sulphides of potassium.

218. The sulphides of metals of the first four groups are practically insoluble in water. **First** and **Second Group** sulphides have small solubility products and the slightly dissociated H_2S serves to precipitate them, even in the presence of acid, while the **Iron** and **Zinc Group** metals require a largely dissociated sulphide, as $(NH_4)_2S$, for complete precipitation. This fact determines the separation of the Silver and Tin and Copper Groups from the Iron and Zinc Groups.

Dilute **acids** decompose soluble sulphides with liberation of H_2S. Dilute HCl dissolves sulphides of iron, manganese and zinc, ZnS less readily than the others; dilute H_2SO_4 dissolves most sulphides. H_2S is made for laboratory use by treatment of FeS with dilute H_2SO_4. Hot dilute HNO_3 decomposes sulphides, except HgS, with oxidation to free S, and, by continued action, to H_2SO_4; H_2S is not liberated: $3CuS + 8HNO_3 = 3Cu(NO_3)_2 + 3S + 2NO + 4H_2O$; $3CuS + 8HNO_3 = 3CuSO_4 + 8NO + 4H_2O$.

H_2S gas is recognized by its **odor** and by its blackening paper moistened with **lead acetate** solution. **Nitroferricyanides,** as **$Na_2FeNO(CN)_5$**, give with the S'' of sulphides, not with H_2S, an intense rich purple color, slowly fading; H_2S must be neutralized. The test is best made on a white porcelain surface, using a few drops of each solution.

219. The sulphur ion of sulphides and of hydrosulphuric acid is a strong reducing agent, acting readily upon **$Fe^{\cdots}$**,

MnO$_4$′, iodine, iodic acid, etc. H_2S burns in air, forming H_2O and SO_2.

Thiosulphuric Acid and Thiosulphates.

220. Thiosulphate (less properly called hyposulphite) of sodium is used in photography as a fixing agent owing to its property of dissolving silver salts; it is called antichlor from its power of converting free Cl into the Cl ion, that is, into hydrochloric acid or a chloride.

Thiosulphuric acid, $H_2S_2O_3$ (sulphuric acid with S substituted for O) breaks down upon formation into H_2SO_3 and S. This change takes place whenever a solution of thiosulphate is acidified, the sulphur being precipitated.

221. Thiosulphates are for the most part soluble in water; those of **Ba**$^{\cdot\cdot}$, **Pb**$^{\cdot\cdot}$, **Hg**$^{\cdot}$, **Hg**$^{\cdot\cdot}$ and **Ag**$^{\cdot}$ are precipitated from solutions not too dilute, all except the Ba salt soon blackening by reduction to sulphide; **As**$^{\cdot\cdot\cdot}$ and **Sb**$^{\cdot\cdot\cdot}$ are precipitated hot as sulphides. Many precipitated thiosulphates form with excess of reagent soluble double thiosulphates of alkali-metal and heavy metal, as $NaAgS_2O_3$. **CaCl$_2$** does not precipitate thiosulphates (separation from sulphites).

222. Thiosulphates are reducing agents; $Na_2S_2O_3$ solution of known strength is used in measuring free **iodine,** which it changes to the colorless I′, the ion of iodides, with formation of tetrathionate: $2I + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6$. Mixed dry with active **oxidizers,** as **chlorates** or **nitrates,** thiosulphates form dangerous explosive mixtures.

Sulphurous Acid and Sulphites.

223. Sulphur dioxide, SO_2, is a colorless gas of the penetrating odor of burning sulphur. It is a reducing agent, and like other strong reducers or oxidizers, it bleaches, breaking up colored organic compounds; it also decolors $KMnO_4$, iodine, etc. It is used as a disinfectant and anti-ferment. One volume of water dissolves about fifty volumes of SO_2;

the solution contains a rather weak acid forming salts derived from H_2SO_3, sulphurous acid.

224. Sulphites of the alkali metals are soluble in water; all others are insoluble and, except Cr, are precipitated by SO_3'', the sulphite ion. The precipitates are soluble in acids, SO_2 going off as gas. Soluble sulphites are decomposed similarly by acid: $Na_2SO_3 + 2HCl = 2NaCl + SO_2 + H_2O$.

Sulphites are identified after precipitation, conveniently with **$BaCl_2$**, by dissolving in **HCl** (separation from $BaSO_4$) and identifying the SO_2 gas liberated on heating by its odor, by passing into **HIO_3**, or by oxidation to sulphate with **Cl**: $2HIO_3 + 5SO_2 + 4H_2O = I_2 + 5H_2SO_4$; and with excess of SO_2: $I_2 + SO_2 + 2H_2O = 2HI + H_2SO_4$. Similarly: $SO_2 + Cl_2 + 2H_2O = 2HCl + H_2SO_4$. The SO_4'' is identified by precipitation as $BaSO_4$, insoluble in HCl.

225. Sulphites are active reducing agents, becoming sulphates: $H_2SO_3 + O = H_2SO_4$. In this way sulphites (SO_3'') reduce **$Fe^{\cdot\cdot\cdot}$** to $Fe^{\cdot\cdot}$, **H_3AsO_4** to H_3AsO_3, **$Hg^{\cdot\cdot}$** to $Hg^{\cdot}$ and then free Hg, **$Ag^{\cdot}$** to free Ag, **IO_3'** to free iodine, and free **iodine** to I'.

With **H_2S** sulphur is precipitated from both acids: $2H_2S + SO_2 = 3S + 2H_2O$.

Sulphuric Acid and Sulphates.

226. Nordhausen or fuming sulphuric acid is made by dissolving SO_3 in H_2SO_4; it deposits crystalline $H_2S_2O_7$ (pyrosulphuric acid), known as solid sulphuric acid.

Pure sulphuric acid is an oily liquid (oil of vitriol) of sp. gr. 1.84. It unites greedily with water, taking it up from the air or other gases, even charring organic bodies by taking from them the elements of water, leaving carbon. As in the case of other acids, in the pure state it is not dissociated and has no acid properties. Dissolved in water it is a fairly strong acid, not so active, however, as the monobasic HNO_3, HCl, $HClO_3$, etc. Like other polybasic acids,

H_2SO_4 dissociates primarily into $H^{\cdot}$ and HSO_4'; the secondary dissociation into $H^{\cdot}$ and SO_4'' is much less extensive.

227. The SO_4 ion, contained in solution of sulphuric acid and its salts, precipitates **$Pb^{\cdot\cdot}$**, **$Ba^{\cdot\cdot}$**, **$Sr^{\cdot\cdot}$**, and in concentrated solution **$Ca^{\cdot\cdot}$** and **$Hg^{\cdot}$**, forming in each case the normal sulphate, white. **Ag_2SO_4** is sparingly soluble, others dissolve readily. **SO_4''** is identified by its precipitation as **$BaSO_4$**, insoluble in dilute HCl.

H_2SO_4 is one of the least volatile of the acids, and so can replace most other acids from their salts. On addition of H_2SO_4 to $NaCl$, for instance, equilibrium sets in between $NaCl$, Na_2SO_4, HCl and H_2SO_4. On heating, the most volatile substance, HCl, is driven off, and in order to restore equilibrium more is formed. The process repeats itself until only Na_2SO_4 and H_2SO_4 remain. This takes place in spite of the fact that HCl is a stronger acid than H_2SO_4. Similarly **phosphoric** or **silicic acid,** less volatile than H_2SO_4, will at high temperatures displace the latter from its salts.

228. The SO_4'' of sulphuric acid and sulphates may act as an oxidizer, undergoing reduction to the sulphite (SO_3'') or even the sulphide ion (S''). Concentrated H_2SO_4 heated with metals, as **Cu** or **Hg**, or with **charcoal** gives off SO_2.

229. Sulphates fused on **charcoal** with Na_2CO_3 form sulphides, blackening a **silver** coin (Ag_2S) brought into contact with the moistened mass. Insoluble sulphates fused with **Na_2CO_3** alone give Na_2SO_4 and an insoluble carbonate: $BaSO_4 + Na_2CO_3 = BaCO_3 + Na_2SO_4$.

Phosphorous.

230. Phosphorus is in the ordinary unstable modification a white translucent solid, melting point 44°, oxidizing rapidly in air, the heat generated soon raising the temperature above the kindling-point, so that the substance is spontaneously inflammable in the air and must be kept under water. Exposed to light it slowly darkens, owing to the formation on the surface of small quantities of the more stable red modification, which is not inflammable below 240° and not poisonous. The element derives its name from its property of giving out light.

Hypophosphorous and Phosphorous Acids and their Salts.

231. Phosphorus treated with alkali or alkaline earth hydroxide solution gives the salt of an oxyacid (hypophosphorous acid) and a hydrogen compound of phosphorus. The reaction is analogous to that of the halogens under similar circumstances, the hydrogen compound of halogen uniting with the base to form a salt: $3Ca(OH)_2 + 8P + 6H_2O = 3CaH_4(PO_2)_2 + 2PH_3$; $2Ca(OH)_2 + 2Cl_2 = Ca(ClO)_2 + CaCl_2 + 2H_2O$.

Hypophosphorous acid is weak; dissociation takes place to a slight extent into $H^{\cdot}$ and H_2PO_2', but goes no further, the second and third hydrogen not splitting off measurably. The only salts formed are accordingly of the type NaH_2PO_2.

Hypophosphites are all soluble in water and cannot be formed by precipitation.

232. Phosphorous acid, H_3PO_3, is weak also, breaking up but little into $H^{\cdot}$ and H_2PO_3', and the latter ion still less into $H^{\cdot}$ and HPO_3'. It does not form salts in which all three hydrogen equivalents have been replaced by metal. The acid salts, as Na_2HPO_3, have alkaline reaction in solution. The phosphites of the alkali metals are soluble, others insoluble in water.

233. Hypophosphites and phosphites are strong reducing agents, the former decoloring the **permanganate** ion immediately, the latter more slowly. **$Hg^{\cdot\cdot}$** is reduced first to $Hg^{\cdot}$ and then to the free metal.

234. Both acids and their salts are decomposed by **heat** with evolution of PH_3, which takes fire owing to the presence of other hydrides of phosphorus, which are spontaneously inflammable.

Phosphoric Acid and Phosphates.

235. Bone-earth or bone-ash, obtained by heating bones, is about 90 per cent normal calcium phosphate and is the chief source of phosphorus compounds. Pyrophosphate of iron, used in medicine, is ferric pyrophosphate, with ammonium citrate to render it soluble. Glacial phosphoric acid is the meta-acid, a wax-like solid.

Phosphoric acid (orthophosphoric), H_3PO_4, is a crystalline solid, deliquescent and going over readily to a syrupy mass. Heat drives off water, leaving pyrophosphoric acid: $2H_3PO_4 - H_2O = H_4P_2O_7$, and this at higher temperatures becomes metaphosphoric acid: $H_4P_2O_7 - H_2O = 2HPO_3$. The anhydride, P_2O_5, formed on burning phosphorus, is a white solid remarkable for the readiness with which it combines with water.

Phosphoric acid is of medium strength, ionized first into $H^{\cdot}$ and H_2PO_4' and then in much slighter degree into $H^{\cdot}$ and HPO_4''. The tendency of the second hydrogen to ionize is so slight that when a dimetallic salt, as Na_2HPO_4, dissolves, the $H^{\cdot}$ of the water is taken up to form non-dissociated H_2PO_4'. The OH' of the water must increase correspondingly, as the product of the two remains always constant, and the result is a solution of alkaline reaction—that is, the dimetallic salt suffers hydrolysis. This hydrolysis is very much greater in the case of a soluble trimetallic phosphate. NaOH added to Na_2HPO_4 solution does not form Na_3PO_4, *i. e.*, the H cannot be separated from the acid radical to unite with OH' and form H_2O; the normal phosphate may, however, be obtained from the solution in the solid state on evaporation, as this removes the water to which hydrolysis was due.

236. The **orthophosphates,** normal and dimetallic, **are insoluble** in water, except those of the common alkalis. Most of them dissolve in H_3PO_4 with formation of soluble dihydrogen phosphates, such as $CaH_4(PO_4)_2$. The precipitates are soluble in the stronger acids, and all except those of **$Fe^{\cdot\cdot\cdot}$**, **$Al^{\cdot\cdot\cdot}$** and **$Pb^{\cdot\cdot}$** in acetic acid; **$Mg^{\cdot\cdot}$** in the presence of NH_4OH forms $MgNH_4PO_4$, crystalline, a very complete precipitation; **$AgNO_3$** gives with normal phosphate yellow Ag_3PO_4, and the resulting solution is neutral in reaction. With acid phosphate (alkaline in reaction) the same precipitate is formed and the solution takes on acid reaction: $Na_3PO_4 + 3AgNO_3 = Ag_3PO_4 + 3NaNO_3$; $Na_2HPO_4 + 3AgNO_3 = Ag_3PO_4 + 2NaNO_3 + HNO_3$.

Metaphosphates precipitate **$Ag^{\cdot}$** as white gelatinous $AgPO_3$; and **pyrophosphates** as white crystalline $Ag_4P_2O_7$; metaphosphoric acid is the only one of the three which precipitates **albumen** from its solution. HPO_3 and $H_4P_2O_7$ both go over slowly in solution into the ortho-acid.

Precipitation takes place when a solution, necessarily acid, containing the radical PO_4 and non-alkali bases, is neutralized. For example, alkaline earth phosphate dissolved in acid is thrown out of solution with Iron Group metals by NH_4OH. For separation see **§132***g*.

Ammonium molybdate, $(NH_4)_2MoO_4$, in its nitric acid solution, precipitates phosphoric acid as canary-yellow ammonium phosphomolybdate, forming more rapidly on warming. Boiling must be avoided as it precipitates from the reagent molybdic acid, white. The reagent must be in excess. For traces set aside several hours.

Boric Acid and Borates.

237. Borax, "biborate" of sodium, is sodium pyroborate, $Na_2B_4O_7,10H_2O$.

The anhydride of boric acid, B_2O_3, forms with varying amounts of water a series of acids similar to those of phosphorus. Orthoboric acid, H_3BO_3, on heating becomes first metaboric, HBO_2, and then pyroboric, $H_2B_4O_7$: $H_3BO_3 - H_2O = HBO_2$; $4HBO_2 - H_2O = H_2B_4O_7$. These acids are all weak and but little dissociated; boric acid is 0.013 per cent dissociated in N/10 solution. Their salts are alkaline in water.

238. The non-alkali borates are insoluble in water and hence alkali borates precipitate salts of most non-alkali bases; **Ag**$^{\cdot}$ is precipitated by $Na_2B_4O_7$ as silver borate; by normal borates as Ag_2O; with **Pb**$^{\cdot\cdot}$, and with **Ba**$^{\cdot\cdot}$ and **Ca**$^{\cdot\cdot}$ not too dilute, white precipitates of normal borates are obtained; with **Al**$^{\cdot\cdot\cdot}$, $Al(OH)_3$.

Borates give a characteristic green **flame** on moistening in an evaporating dish with H_2SO_4, adding alcohol, warming, and then setting fire to the alcohol. Or if a dry powdered borate is moistened with H_2SO_4, heated in the loop of platinum wire to expel the acid and then moistened with glycerine the glycerine will burn with green flame. Copper must be removed before making these tests.

Paper colored yellow with **turmeric**, an organic coloring agent, is changed to reddish brown by dipping into solution of H_3BO_3 or of a borate faintly acidulated with HCl, and drying.

239. Borates in the inner **blowpipe flame** give the green color to the outer flame.

Silicic Acid and Silicates.

240. The anhydride of silicic acid, SiO_2, silica, is nearly pure in rock crystal and is the substance of quartz, agate, chalcedony, flint and sand, and enters into the composition of a great number of minerals, the silicates. Glass contains silicates of Ca, Na, Pb, K, etc., and silica; porcelain is made from fine clay, a silicate of aluminum; soluble glass, water-glass, is sodium or potassium silicate; carborundum is SiC.

Silica is the anhydride of a number of very weak acids, H_4SiO_4, H_2SiO_3 and others. These acids form colloid solutions from which they are precipitated more or less completely in gelatinous form on addition of non-alkaline electrolytes (salts or acids); this precipitation takes place on addition of NH_4Cl for the Iron Group.

241. Silicates of the alkali metals are soluble, others insoluble. The soluble compounds are formed from insoluble silicates or silica: (1) by long fusion in a crucible with a mixture of sodium and potassium carbonates, the mixture, as in the case of all mixtures or impure substances, melting at a lower temperature than the single pure substance; or (2) by boiling with solution of fixed alkali hydroxide in a bright iron or silver dish. The mass after fusion or the solution in alkali hydroxide is treated with HCl in excess (that is, to acid reaction), the silicic acid dissolving as a colloid. The bases of the original silicates will in most cases also dissolve as chlorides. To test for silica this acid solution, filtered if necessary, is evaporated and dried at 100-110° C. The dried mass is treated with HCl. A residue not dissolving in the acid, gritty under the glass rod, is silica.

Silica and silicates are attacked by **HF**, with formation of volatile SiF_4. This passed into water is decomposed into gelatinous silicic acid and hydrosilicofluoric acid: $3SiF_4 + 3H_2O = H_2SiO_3 + 2H_2SiF_6$.

242. In the fused bead of **microcosmic salt** silica swims undissolved. The base of a silicate dissolves, leaving the skeleton of silica.

Examination for the Anions of Volatile Acids.

243. To a little of the solid substance or residue by evaporation add concentrated H_2SO_4 and heat gently.

A **colorless odorless gas,** giving a white precipitate on passing into $Ca(OH)_2$ solution, is **CO_2, from carbonates.** Solutions of carbonates precipitate all bases except the alkalis. **Oxalates** with concentrated H_2SO_4, not with dilute, slowly evolve CO_2: $H_2C_2O_4 = H_2O + CO_2 + CO$.

A **colorless gas having odor** and bleaching or reddening moist litmus-paper may be:

H_2S, from **sulphides.** Gas blackens paper wet with lead acetate. Sulphides precipitate the kathions of the first four groups.

SO_2, from **sulphites.** Odor of burning sulphur. Litmus-paper is bleached. **Gas liberates iodine from iodic acid.** Sulphites precipitate all kathions except the alkali-metals. SO_2 is also given off by thiosulphates, with separation of sulphur. $Ca^{\cdot\cdot}$ is not precipitated by thiosulphates (distinction from sulphites).

HCN, from **cyanides.** Poisonous. Has peach-blossom odor. Precipitates $AgNO_3$ solution on a glass rod, precipitate insoluble in HNO_3, decomposed by strong HCl with evolution of HCN. Changed to sulphocyanate, gives blood-red with $Fe^{\cdots}$. For production of HCN from ferrocyanides, see §**202**.

$HC_2H_3O_2$, from **acetates.** Vinegar odor. Acetic ether test. With $Fe^{\cdots}$ red solution (§**214**). Acetates are all soluble in water.

HCl, from **chlorides.** Slight effervescence. Gas is irritating when inhaled. Precipitates $AgNO_3$ solution on glass rod, the precipitate insoluble in HNO_3. Cl' precipitates Silver Group kathions.

A **colored** gas may be:

HI and **I**, from **iodides.** Odor resembling that of chlorine. Violet color due to the free iodine. Test in dilute solution with chlorine-water (§186). I' precipitates Silver-Group kathions, $Hg^{\cdot\cdot}$, $Cu^{\cdot\cdot}$ (as $Cu^{\cdot}$) and $Cu^{\cdot}$.

HBr with **Br**, from **bromides.** Slight yellowish-brown color, due to small quantity of free bromine. Odor acrid and chlorine-like. Test solution with chlorine-water. Silver Group kathions and oxy-salts of $Hg^{\cdot\cdot}$ are precipitated by Br'.

NO_2, nitrogen peroxide, brownish-red color, characteristic odor. Formed by action of air on **NO**, which is liberated from **nitrites** on treatment with acids, and from **nitrites** or **nitrates** on heating to sufficiently high temperature.

ClO_2, from **chlorates.** Greenish-yellow. Chlorine-like odor. Crackling or explosion. Litmus bleached. No precipitates. See §178.

Cl_2, from **hypochlorites.** Original material in solution bleaches litmus. See §175.

A gas which is not perceptible except by its irritating properties may be:

HNO_3, from **nitrates.** Brown-ring test, etc. (§193). No precipitates.

HF, from fluorides. Etching test (§168).

Examination for Anions (Radicals) of Non-Volatile Acids.

244. For **SiO_3'' (silicic acid)**: Fuse with alkali carbonates, acidulate, evaporate dry, take up with acidulated water (§241). Bead test (§242).

For **BO_3'' (boric acid)**: Flame test (§237).

For **$Fe(CN)_6''''$ (hydroferrocyanic acid)**: In solution test with $Fe^{\cdot\cdot\cdot}$. If insoluble in water digest with KOH, filter and test filtrate.

For **$Fe(CN)_6'''$ (hydroferricyanic acid)**: Test solution with $Fe^{\cdot\cdot}$. If not soluble in water treat with NaOH and test filtrate.

For **CNS' (sulphocyanic acid)**: Test with $Fe^{\cdot\cdot\cdot}$ (§205).

For the Ions SO_4'', C_2O_4'', PO_4''' of Sulphates, Oxalates and Phosphates.

245. Acidify the solution slightly with **HCl**, boil to drive off **CO_2**, **SO_2**, etc., and add **$BaCl_2$**. A white precipitate is **$BaSO_4$** [or **$BaSiF_6$**].

Filter, add $CaCl_2$ and NH_4OH to alkaline reaction. Precipitate: **CaC_2O_4**, **$Ca_3(PO_4)_2$** (also **borate, silicate, fluoride, chromate, arsenate, iodate, ferrocyanide, molybdate** of **barium** and **calcium**).

Filter; reject filtrate; treat precipitate with **acetic acid.**

Residue, **CaC_2O_4**, white. Dissolve in dilute **HNO_3**, add dilute **$KMnO_4$** solution, pass gas liberated into **$Ca(OH)_2$** solution. A white precipitate (**$CaCO_3$**) is evidence of the presence of **oxalate**.	Solution, **H_3PO_4**, **$Ca(C_2H_3O_2)_2$**. Add **ammonium molybdate**; warm slightly; yellow precipitate, **ammonium phosphomolybdate.** **AsO_4'''** gives a very similar precipitate, and must be removed by **H_2S**, boiling off excess, before the tests in this table are made.

For the Ions Cl′, Br′, I′, etc., of Chlorides, Bromides, Iodides and other Salts forming Insoluble Silver Compounds.

246. Add to the solution **$AgNO_3$**. In neutral solution most anions will be precipitated, as but few silver salts are soluble. Digest with hot dilute **HNO_3**. Filter and wash.

Residue: **AgI**, **AgBr**, **AgCl**, **AgCN**, **AgCNS**, **Ag_2CrO_4**,* **$AgIO_3$**.*

Treat with warm **NH_4OH** on the filter.

Residue: **AgI** and some **AgBr**. **Test original solution for I′ and Br′.**	Filtrate: Soluble **chloride, bromide, cyanide, sulphocyanate, [chromate, iodate] of complex silver-ammonium kathions.** Add **HNO_3** to slight acid reaction. Precipitate: **AgBr, AgCl, AgCN, AgCNS [Ag_2CrO_4, $AgIO_3$].** For **chloride** in presence of **bromide** apply **chlorochromic** test (§172) to original substance; in presence of CN′ or CNS′ boil precipitate with concentrated **H_2SO_4**. **AgCN** and **AgCNS** decompose and dissolve; **AgCl** is unaffected.

247. The presence of a certain kathion in neutral solution excludes the presence of those anions with which it forms salts insoluble in water; Ag˙, for instance, excludes Cl′, Br′, I′, etc. It is well to test for the kathions first; the result shows what anions need not be tested for. Certain kathions interfere with tests for anions. Silver Group kathions, for instance, give, when the test for SO_4'' is made, a white precipitate with $BaCl_2$ but little soluble in HCl and likely to be mistaken for $BaSO_4$. Under such circumstances another reagent must be used, here $Ba(NO_3)_2$, or the interfering kathions must be removed, in this case by HCl or H_2S. Kathions should not be removed before testing for

* The chromate and iodate are soluble in much HNO_3.

anions unless it is necessary. This must be determined in each case by a careful consideration of the effect of the reagent to be used on the kathion known to be present.

Bead-Tests.

248. The loop of platinum wire, red hot, is dipped into powdered microcosmic salt,* $NaNH_4HPO_4$, or borax, $Na_2B_4O_7$, which is then fused to a clear bead. The hot bead is brought into contact with a very little of the substance under examination (in powder) and fused again until clear, first in the outer, oxidizing Bunsen or blowpipe flame, then in the inner or reducing flame. A suitable reducing flame is obtained with the Bunsen burner by shutting off the air supply until a small luminous spot appears within the flame; the substance is heated in this. Certain metallic oxides dissolve in these beads with characteristic colors, for the most part the same whether borax or microcosmic salt be used. Silica remains undissolved in the microcosmic salt bead but dissolves in the borax bead.

Iron gives a yellow to brown or red bead in the oxidizing flame, green in the reducing flame.

Copper, green when hot, blue when cold, in the oxidizing flame; red (opaque when in excess) in the reducing flame.

Chromium is green in oxidizing or reducing flame.

Cobalt is blue in oxidizing or reducing flame.

Nickel is red in oxidizing flame; mixed with cobalt violet.

Manganese is violet or amethyst in oxidizing flame, colorless in reducing flame.

Treatment of Solids.

249. To dissolve a solid it is reduced to a powder and, first, boiled with about ten times its bulk of water. Should a residue (a) remain it is allowed to subside and the clear liquid poured off or separated by filtration. The action of this liquid on indicators is noted and it is tested for the kathions and anions. A drop or two evaporated on platinum foil shows to what extent the solid has dissolved. The residue (a) is exhausted and washed with hot water.

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* Sodium metaphosphate $NaPO_3$, may as well or better be used. $NaNH_4HPO_4$ on heating forms $NaPO_3$, NH_3, and H_2O.

2. Take a small portion of residue (a) and treat with HCl; if it does not dissolve take another small portion and treat with HNO_3. The entire residue is treated with that acid which dissolves it more readily. Any gas given off should be identified. The mixture is evaporated almost dry, taken up with hot water, and any insoluble residue (b) filtered out.

A residue insoluble in strong acid ($BaCl_2$, $Pb(NO_3)_2$, etc.) may dissolve in water, and on the other hand water may cause precipitation of substances held in solution by strong acid. If the acid solution, clear originally, becomes turbid on evaporating and taking up with water it may have contained AgCl (soluble in HCl), insoluble sulphates, silica, or salts of $Cu^{\cdot}$, Bi, Sb, Sn or Hg. If the turbidity, as is perhaps usually the case, is due to metals of the Tin and Copper Group only, filtration is unnecessary and the H_2S may be passed directly into the turbid solution.

Peroxides, as MnO_2 or PbO_2, dissolve in HCl with liberation of chlorine; they dissolve in HNO_3 only if a reducing agent, as pure H_2O_2, or alcohol, or a small crystal of $H_2C_2O_4$ is added.

The separation of sulphur on treatment with HNO_3 indicates a sulphide (or thiosulphate); NO gas, changing to brown NO_2, indicates oxidation of a metal or other substance.

3. The residue (b) is washed and treated either with HNO_3 or HCl, the acid not used for the previous solution. The solution so obtained is treated precisely as the foregoing.

4. If a residue still remains it is washed and treated with nitrohydrochloric acid and the solution evaporated and examined as before.

5. Should the substance prove insoluble in acids it is likely

to be an insoluble sulphate, chloride, bromide, silicate or fluoride, an oxide of tin or antimony, or sulphur or carbon; and it must be heated to quiet fusion in a crucible with four times its weight of a mixture of equal parts Na_2CO_3 and K_2CO_3. The fused mass is extracted with water; the anion of the insoluble substance will be found in the solution, and the residue, soluble in acid, contains the kathion: $BaSO_4 + Na_2CO_3 = BaCO_3 + Na_2SO_4$.

Oxides of antimony and tin are better dissolved after fusion with three times their weight of alkali carbonates and the same quantity of sulphur. Sulpho-salts form, soluble in water.

Alkali metals are detected in insoluble silicates by heating to bright red for almost an hour with an equal weight of NH_4Cl and eight times the quantity of $CaCO_3$. The mass is taken up with water, filtered, and after completely removing $Ca^{\cdot\cdot}$ with $(NH_4)_2CO_3$ the filtrate is examined in the usual way for the alkali metals.

250. Group Separations.

Add HCl a drop at a time as long as a precipitate is produced; shake and filter.

<table>
<tr>
<td rowspan="5">Precipitate:
Silver Group.
$PbCl_2$, white
HgCl, white
AgCl, white
§ 84.</td>
<td colspan="5">Neutralize filtrate with NH_4OH, disregarding a precipitate, acidify slightly with HCl, warm and pass H_2S gas. Filter.</td>
</tr>
<tr>
<td rowspan="4">Precipitate:
Tin and Copper Group.
As_2S_3 and As_2S_5, yellow
Sb_2S_3 and Sb_2S_5, orange
SnS, brown
SnS_2, yellow
HgS, black
PbS, black
Bi_2S_3, black
CuS, black
CdS, yellow
§ 87 and § 89.</td>
<td colspan="4">Filtrate: Expel H_2S by boiling, add a little HNO_3, boil, add NH_4Cl and NH_4OH. Filter.</td>
</tr>
<tr>
<td rowspan="3">Precipitate:
Iron Group.
$Fe(OH)_3$, brown
$Cr(OH)_3$, grayish-green
$Al(OH)_3$, white, gelatinous
§ 110.</td>
<td colspan="3">Filtrate: Pass H_2S gas. Filter.</td>
</tr>
<tr>
<td rowspan="2">Precipitate:
Zinc Group.
CoS, black
NiS, black
MnS, flesh-colored
ZnS, white
§ 131.</td>
<td colspan="2">Filtrate: Add NH_4OH and $(NH_4)_2CO_3$, warm, and filter.</td>
</tr>
<tr>
<td>Precipitate:
Alkaline Earth Group.
$BaCO_3$, white
$SrCO_3$, white
$CaCO_3$, white
§ 146.</td>
<td>Filtrate: Contains Mg of the Alkaline Earth Group (§ 146), and the Alkali Group § 164.</td>
</tr>
</table>

Table of Solubilities.

	Silver.	Lead.	Mercurous.	Antimonous.	Stannous.	Stannic.	Mercuric.	Bismuth.	Cupric.	Cadmium.	Ferrous.	Ferric.	Chromium.	Aluminum.	Cobalt.	Nickel.	Manganese.	Zinc.	Barium.	Strontium.	Calcium.	Magnesium.	Ammonium.	Sodium.	Potassium.
Arsenate	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	2	1	1	1		4	4
Arsenite	1	2	1	1			1		1		1	1			1	1	1		2	2	1	1	4	4	4
Bromide	1	2	1	h	h	h	2	h	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4
Carbonate	1	1	1	1	1	1	1	1	1	1	1				1	1	1	1	1	1	1	1	4	4	4
Chlorate	3	4	4				h		4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	3
Chloride	1	2	1	h	h	h	3	h	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4
Chromate	1	1	1	1	1	1	1	1	1	1		1	1	1	1	1	1	1	1	2	2	4	4	4	4
Cyanide	1	1	1				4	2	1	1	1		1		1	1	1	1	2	4	4	4	4	4	4
Ferricyanide	1	2	1		1		1	1	1	1	1	4			1	1	1		2		4	4	4	4	4
Ferrocyanide	1	1		1	1	1		2	1	1	1	1	1	2	1	1	1	1	2	4	4	4	4	4	4
Hydroxide		1		1	1	1		1	1	1	1	1	1	1	1	1	1	1	3	3	2	1	4	4	4
Iodide	1	2	2	h	h	h	1	h		4	4		4	4	4	4	4	4	4	4	4	4	4	4	4
Nitrate	4	4	h	h	h	h	h	h	4	4	4	4	4	4	4	4	4	4	3	4	4	4	4	4	4
Oxide	2	1	1	1	1	1	2	1	1	1	1	1	1	1	1	1	1	1	3	3	2	1			
Phosphate	1	1	1	2	1	1	2	1	1	1	1	1	1	1	1	1	1	1	1	1	1	2	4	4	4
Sulphate	2	1	2	h	h	h	h	h	4	4	4	4	4	4	3	4	4	4	1	1	2	4	4	4	4
Sulphide	1	1	1	1	1	1	1	1	1	1	1	1	1	h	1	1	1	1	h	h	h	h	4	4	4

Solubilities—continued.

Ammonium platinichloride	2	Potassium bromate	3
Arsenous oxide	3	Potassium dichromate	3
Barium iodate	2	Potassium iodate	3
Barium silicofluoride	2	Potassium perchlorate	3
Calcium sulphite	2	Potassium permanganate	3
Cuprous bromide	1	Potassium platinichloride	2
Cuprous chloride	2	Silver chlorate	3
Cuprous iodide	1	Sodium bicarbonate	3
Lithium carbonate	2	Sodium iodate	3
Lithium phosphate	2	Sodium pyroborate	3
Potassium bitartrate	2		

Key to Table of Solubilities.

1. Insoluble in water. Substances so designated dissolve as a rule to less than 0.100 gram in one liter of water.

2. Slightly soluble; usually from 0.100 gram to 10 grams per liter.

3. Moderately soluble; from 10 to about 100 grams per liter.

4. Freely soluble; above 100 grams per liter.

h. Hydrolyzed and not dissolved by water alone, but soluble in acidulated water.

252. *Reagents.*

Acids.

Concentrated sulphuric acid, H_2SO_4, nearly or quite absolute (*i. e.*, free from water), sp. gr. 1.84.

Dilute sulphuric acid, 5N, 245 grams per liter, sp. gr. 1.153. Add 1 volume of acid, gradually and with stirring, to about seven volumes of water.

Acetic acid, $HC_2H_3O_2$, 5N, 300 grams per liter, sp. gr. 1.04.

Hydrochloric acid, HCl, 5N, 182 grams per liter, sp. gr. 1.084. Three volumes water to two volumes HCl sp. gr. 1.20.

Hydrosulphuric acid, H_2S. Saturated water solution, about N/6. Applied better for most purposes as the gas, generated by action of dilute sulphuric acid on ferrous sulphide.

Nitric acid, HNO_3, 5N, 315 grams per liter, sp. gr. 1.165. 225 cc. water to 100 cc. HNO_3 sp. gr. 1.42.

Nitrohydrochloric acid. A mixture, made when wanted, of three volumes reagent hydrochloric to one volume reagent nitric. The nitric acid liberates chlorine from the hydrochloric and the mixture owes its efficacy to the fact that it combines oxidizing power with the ability to form such stable compounds as chlorides.

Bases.

Ammonium hydroxide, NH_4OH, 5N, 85 grams NH_3 per liter, sp. gr. 0.964. Two volumes water to one volume NH_4OH sp. gr. 0.90.

Calcium hydroxide, $Ca(OH)_2$, saturated water solution, about N/20.

Potassium hydroxide, KOH, 5N, 312 grams per liter of the solid containing about 90 per cent KOH.

Sodium hydroxide, $NaOH$, 5N, 220 grams per liter of the solid containing about 90 per cent NaOH.

Salts.

Ammonium carbonate, $(NH_4)_2CO_3$, 5N, 240 grams per liter. Dissolve one part of the crystallized salt, $NH_4HCO_3,NH_4CO_2NH_2$, in 4 parts water and one part reagent NH_4OH.

Ammonium chloride, NH_4Cl, 3N, 160 grams per liter.

Ammonium molybdate. The solution contains molybdic acid, about $\frac{2}{3}$N, ammonium nitrate and nitric acid. It is made by dissolving 100 grams MoO_3 in 250 cc. NH_4OH sp. gr. 0.90 and 250 cc. water, and slowly pouring this, stirring, into a mixture of 750 cc. HNO_3 sp. gr. 1.42 and 750 cc. water.

Ammonium oxalate, $(NH_4)_2C_2O_4,2H_2O$, N/2, 40 grams per liter.

Ammonium sulphide, colorless, $(NH_4)_2S$. Saturate ammonium hydroxide solution with H_2S, forming NH_4HS, and add an equal volume of the ammonium hydroxide solution.

Ammonium sulphide, yellow, $(NH_4)_2S_x$, is made from the above by dissolving sulphur in it.

Barium chloride, $BaCl_2,2H_2O$, N/2, 61 grams per liter.

Calcium chloride, $CaCl_2,6H_2O$, N/2, 55 grams per liter.

Calcium sulphate, $CaSO_4,2H_2O$, saturated water solution, about N/43.

Ferric chloride, $FeCl_3$, N/2, 27 grams per liter.

Ferrous sulphate, $FeSO_4,7H_2O$, N/2, 80 grams per liter. Add a few drops of H_2SO_4 to dissolve basic ferric salt.

Lead acetate, $Pb(C_2H_3O_2)_2,3H_2O$, N/2, 95 grams per liter.

Magnesia mixture (Mg about 4/3N), $MgSO_4$, 100 grams, NH_4Cl 200 grams, NH_4OH 400 cc., H_2O 800 cc.

Mercuric chloride, $HgCl_2$, N/2, 68 grams per liter.

Potassium chlorate (free from chloride), $KClO_3$, saturated water solution, about N/2.

Potassium cyanide, KCN, N/2, 33 grams per liter.

Potassium dichromate, $K_2Cr_2O_7$, N/4, 38 grams per liter.

Potassium ferricyanide, $K_3Fe(CN)_6$, N/2, 55 grams per liter.

Potassium ferrocyanide, $K_4Fe(CN)_6,3H_2O$, N/2, 53 grams per liter.

Potassium iodate, KIO_3, N/2 (as to oxidizing capacity), 18 grams per liter.

Potassium iodide, KI, N/2, 83 grams per liter.

Potassium mercuri-iodide, K_2HgI_4, Nessler's reagent: Heat 35 grams KI and 13 grams $HgCl_2$ with 800 cc. water, stirring until a clear solution results. Add drop by drop a saturated solution of $HgCl_2$ until a slight permanent precipitate is obtained. 160 grams KOH or 120 grams NaOH are now added, the whole diluted to a liter, a little more $HgCl_2$ solution added, and the liquid allowed to settle (Fresenius).

Potassium sulphocyanate, $KCNS$, N/2, 49 grams per liter.

Potassium sulphate, K_2SO_4, N/2, 44 grams per liter.

Silver nitrate, $AgNO_3$, N/4, 43 grams per liter.

Sodium carbonate, Na_2CO_3, 3N, 159 grams per liter.

Sodium hydrogen phosphate, $Na_2HPO_4.12H_2O$, N/2, 60 grams per liter.

Stannous chloride, $SnCl_2.2H_2O$, N/2, 56 grams per liter. HCl must be added to prevent precipitation.

A half-normal solution of at least one salt of each of the common metals should also be prepared and kept accessible for use in obtaining the reactions of kathions and anions as known substances, and for purposes of comparison.

Miscellaneous.

Alcohol, C_2H_5OH, sp. gr. 0.815, about 95 per cent.

Carbon disulphide, CS_2, colorless.

Diphenylamine: Dissolve in concentrated H_2SO_4.

Hydrogen peroxide, 3 per cent solution.

Indigo solution: Dissolve one part of finely pulverized indigo in small portions in five parts fuming H_2SO_4, cooling and stirring. Let stand 48 hours, pour into 20 parts water and filter (Fresenius).

Nitroso-β-naphthol: Dissolve in 50 per cent acetic acid.

Summary of Precipitations.

Fixed alkali carbonates (the **CO_3 ion** in large concentration) precipitate the kathions of all other metals (not $As^{\cdot\cdot\cdot}$). The precipitate is an oxide with $Sb^{\cdot\cdot\cdot}$, a hydroxide with $Sn^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, $Cr^{\cdot\cdot\cdot}$ and $Fe^{\cdot\cdot\cdot}$; with antimonic compounds it is antimonic acid, H_3SbO_4, with stannic compounds stannic acid, H_2SnO_3, and in other cases a normal or basic carbonate, except for $HgCl_2$, which forms an oxychloride.

Metallic oxides and hydroxides are insoluble, except those of the alkali-metals; those of Ba, Sr and Ca are slightly soluble. **Fixed alkali hydroxides** (the **OH ion** in large concentration) precipitate the kathions of the common metals (not $As^{\cdot\cdot\cdot}$). The precipitate is a hydroxide, except that $Ag^{\cdot}$, $Sb^{\cdot\cdot\cdot}$, $Hg^{\cdot}$ and $Hg^{\cdot\cdot}$ form the oxides, antimonic compounds form antimonic acid, H_3SbO_4, and stannic compounds form stannic acid, H_2SnO_3. The precipitate redissolves in excess of the reagent in the cases of Pb, Sn, Sb, Cr, Al and Zn; $Cr(OH)_3$ is reprecipitated on boiling the alkaline solution.

Ammonium hydroxide solution (the **OH ion** in slight concentration) precipitates kathions of the first four analytical groups (not $As^{\cdot\cdot\cdot}$); $Fe^{\cdot\cdot}$, $Mn^{\cdot\cdot}$ and $Mg^{\cdot\cdot}$ are precipitated but partially or not at all in the presence of ammonium salts (the ion $NH_4^{\cdot}$). The precipitate is a hydroxide except with $Ag^{\cdot}$ and $Sb^{\cdot\cdot\cdot}$, which form the oxides, with $Pb^{\cdot\cdot}$, which forms a basic salt, with $Hg^{\cdot\cdot}$, which forms mercuric ammonium compounds, and with $Hg^{\cdot}$, which forms mercuric ammonium compounds and free Hg. The precipitate redissolves in excess of the reagent in the cases of Ag, Cu, Cd, Co, Ni and Zn.

The sulphides of the kathions of the first four groups are insoluble in water, those of the first two groups insoluble also in dilute acid. **H_2S** (the **S ion** in slight concentration) precipitates in the presence of dilute acid the kathions of the first two groups as sulphides. It reduces $Fe^{\cdot\cdot\cdot}$, Cr_2O_7'',

MnO_4' (the ferric, dichromate and permanganate ions), etc., with precipitation of sulphur only.

Soluble **sulphides**, or H_2S in alkaline solution (the **S ion** in considerable concentration) precipitate the kathions of the first four groups as sulphides, except $Al^{\cdot\cdot\cdot}$ and $Cr^{\cdot\cdot\cdot}$, which are precipitated as hydroxides, and $Fe^{\cdot\cdot\cdot}$, which forms FeS and S.

Solution of **sulphuric acid** or a **sulphate** (the **ion SO_4''**) precipitates $Pb^{\cdot\cdot}$, $Ba^{\cdot\cdot}$, $Sr^{\cdot\cdot}$, and from concentrated solution $Hg^{\cdot}$, $Ag^{\cdot}$ and $Ca^{\cdot\cdot}$, all as the sulphates.

Solution of **hydrochloric acid** or a **chloride** (the **ion Cl'**) precipitates $Ag^{\cdot}$, $Hg^{\cdot}$ and $Pb^{\cdot\cdot}$ as the chlorides, $Pb^{\cdot\cdot}$ incompletely. **Hydrobromic acid** and **bromides** (the **ion Br'**) precipitate the bromides in the same cases.

Solution of **hydriodic acid** or an **iodide** (the **ion I'**) precipitates $Ag^{\cdot}$, $Hg^{\cdot}$, $Pb^{\cdot\cdot}$, $Hg^{\cdot\cdot}$ and $Cu^{\cdot}$ as the iodides, $Cu^{\cdot\cdot}$ as CuI with liberation of iodine. $Fe^{\cdot\cdot\cdot}$ becomes $Fe^{\cdot\cdot}$ and H_3AsO_4 becomes H_3AsO_3, with liberation of iodine.

Atomic Weights.*

	H = 1.	O = 16.
Aluminum, Al	26.9	27.1
Antimony, Sb	119.5	120.4
Argon, Ar	40. ?	40. ?
Arsenic, As	74.45	75.0
Barium, Ba	136.4	137.40
Beryllium, Be. See Glucinum.		
Bismuth, Bi	206.5	208.1
Boron, B	10.9	11.0
Bromine, Br	79.34	79.95
Cadmium, Cd	111.55	112.4
Caesium, Cs	131.9	132.9
Calcium, Ca	39.8	40.1
Carbon, C	11.9	12.0
Cerium, Ce	138.0	139.0
Chlorine, Cl	35.18	35.45
Chromium, Cr	51.7	52.1
Cobalt, Co	58.55	59.00
Columbium, Cb	93.0	93.7
Copper, Cu	63.1	63.6
Erbium, Er	164.7	166.0
Fluorine, F	18.9	19.05
Gadolinium, Gd	155.8	157.0
Gallium, Ga	69.5	70.0
Germanium, Ge	71.9	72.5
Glucinum, Gl	9.0	9.1
Gold, Au	195.7	197.2
Helium, He	4. ?	4. ?
Hydrogen, H	1.000	1.008
Indium, In	113.1	114.0
Iodine, I	125.89	126.85
Iridium, Ir	191.7	193.1
Iron, Fe	55.5	55.9
Krypton, Kr	59. ?	59. ?
Lanthanum, La	137.6	138.6
Lead, Pb	205.36	206.92
Lithium, Li	6.97	7.03
Magnesium, Mg	24.1	24.3
Manganese, Mn	54.6	55.0
Mercury, Hg	198.50	290.0

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* F. W. Clarke, Jour. Am. Chem. Soc., 1901, 23, 90.

	H=1.	O=16.
Molybdenum, Mo.	95.3	96.0
Neodymium, Nd.	142.5	143.6
Neon, Ne.	20.?	20. ?
Nickel, Ni.	58.25	58.70
Niobium, Nb. **See Columbium.**		
Nitrogen, N.	13.93	14.04
Osmium, Os.	189.6	191.0
Oxygen, O.	15.88	16.000
Palladium, Pd.	106.2	107.0
Phosphorus, P.	30.75	31.0
Platinum, Pt.	193.4	194.9
Potassium, K.	38.82	39.11
Praseodymium, Pr.	139.4	140.5
Rhodium, Rh.	102.2	103.0
Rubidium, Rb.	84.75	85.4
Ruthenium, Ru.	100.9	101.7
Samarium, Sm.	149.2	150.3
Scandium, Sc.	43.8	44.1
Selenium, Se.	78.6	79.2
Silicon, Si.	28.2	28.4
Silver, Ag.	107.11	107.92
Sodium, Na.	22.88	23.05
Strontium, Sr.	86.95	87.60
Sulphur, S.	31.83	32.07
Tantalum, Ta.	181.5	182.8
Tellurium, Te.	126.5	127.5 ?
Terbium, Tr.	158.8	160.
Thallium, Tl.	202.61	204.15
Thorium, Th.	230.8	232.6
Thulium, Tm.	169.4	170.7
Tin, Sn.	118.1	119.0
Titanium, Ti.	47.8	48.15
Tungsten, W.	182.6	184.
Uranium, U.	237.8	239.6
Vanadium, V.	51.0	51.4
Xenon, X.	?	?
Ytterbium, Yb.	171.9	173.2
Yttrium, Y.	88.3	89.0
Zinc, Zn.	64.9	65.4
Zirconium, Zr.	89.7	90.4

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